J. Bangladesh Acad. Sci.50(2); 315–327: June 2026 DOI: https://doi.org/10.3329/jbas.v50i2.90661

Journal of Bangladesh Academy of Sciences

Journal homepage: http://www.bas.org.bd/publications/jbas.html

Research Article

Axial substitution and antibacterial activities of cobalt(III) complexes of an octamethyl substituted tetraaza macrocyclic ligand

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ARTICLE INFO

Article History

Received: 24 February 2026
Revised: 19 May 2026
Accepted: 19 May 2026

Keywords: Macrocyclic ligand, N-pendent derivative, Co(III) complexes, Axial substitution, Spectroscopy, Antibacterial activity.

ABSTRACT

Six-coordinate cobalt(III) complexes containing octamethyl-substituted tetraazamacrocyclic ligand Me_8[14]diene have been synthesized and characterized. The trans-dichlorido diastereomeric complexes, *trans*-$[CoL_\alpha Cl_2](ClO_4)$ and *trans*-$[CoL_\beta Cl_2](ClO_4)$, were obtained via aerial oxidation of the solution containing ligand and Co(II)-salt, with the addition of HCl & $HClO_4$. Subsequently, the precursor diastereoisomer *trans*- $[CoL_\alpha Cl_2](ClO_4)$ underwent axial substitution reactions with NO_3^-, NO_2^-, SCN^-, Br^-, and I^- ions to afford a range of cobalt(III) trans-derivatives. CHN analysis, conductance analysis, infrared, proton, carbon-13 nuclear magnetic resonance, electronic spectroscopic methods, and magnetic susceptibility were used to characterize these complexes. Analytical results have proven the presence of a d^6 low spin metal ion cobalt(III) in an octahedral environment, where the macrocycle occupies an equatorial plane while anions occupy an axial plane. Conductometric studies suggest the electrolytic properties of the complexes. The biological activities of the complexes in terms of their antibacterial properties were tested for selected Gram-positive and Gram-negative bacteria, showing that they have moderate-to-poor efficacy against these bacteria in comparison with a reference drug like ampicillin and increased effectiveness in comparison with the free ligand. This is very useful in explaining how cobalt(III) undergoes axial substitution under tetraazamacrocyclic conditions, which further goes to show how the presence of anion ligands affects their physicochemical and biological properties.

Introduction

Macrocyclic compounds which contain several nitrogen donating atoms play an important role in coordination chemistry owing to their predefined cavity structure, excellent complexation properties and selective binding of transition metal ions. The enhanced thermodynamic stability and kinetic inertness of their complexes, commonly described as the macrocyclic effect-enable stabilization of metal ions in defined oxidation states and geometries (Cabbiness and Margerum, 1969; Busch, 1978). These features make multiazamacrocyclic systems valuable platforms for investigating structure–reactivity relationships in inorganic and bioinorganic chemistry.

Cobalt(III) is particularly suitable for such investigations because of its low-spin d^6

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configuration, which typically affords diamagnetic, octahedral, and kinetically inert complexes. The rigidity of Co(III)–macrocycle frameworks allows systematic probing of axial ligand effects without perturbation of the equatorial coordination plane. Variations in axial ligation provide mechanistic insight into ligand field strength, electronic transitions, substitution behavior, and anion lability (Lever, 1972; Tobe, 1972; Hay and Pujari, 1980; Hathaway, 1984). Such studies are essential for correlating coordination environment with spectroscopic and physicochemical properties. In addition to their fundamental chemical significance, macrocyclic metal complexes have demonstrated promising pharmacological potential, including antibacterial, antifungal, anticancer, and therapeutic activities (Singh and Kumar, 2007; Chandra and Kumar, 2005; Tweedy, 1964; Gupta and Sutar, 2008). The nature of coordinated axial ligands often modulates lipophilicity, charge distribution, and biological interaction pathways, thereby influencing antimicrobial performance. Consequently, systematic axial substitution studies in cobalt(III) macrocyclic systems are both chemically and biologically relevant.

Octamethyl-substituted 14-membered tetraazamacrocycles, such as Me_8[14]diene, provide a sterically constrained and electronically tunable ligand environment. The methyl substituents impose conformational rigidity, potentially leading to distinct diastereomeric arrangements and controlled axial coordination. However, comprehensive studies on cobalt(III) complexes (Rabi et al., 2016; Roy et al., 2011; Roy et al., 2011; Roy et al., 2006; Kumar et al., 2020; Ho et al., 2019; Kumar and Chandra, 2010; Khaled et al., 2006; Hay and Jeragh, 1977) derived from the free ligand Me_8[14]diene (L) (Roy et al., 2006), particularly focusing on systematic axial substitution and associated biological implications, remain limited.

Despite extensive investigations of cobalt(III) macrocyclic systems, a clearly defined understanding of how steric constraints imposed by octamethyl-substituted tetraazamacrocycles influence axial substitution behavior and related biological activity remains incomplete. In particular, systematic studies focusing on cobalt(III) complexes derived from Me_8[14]diene (Roy et al., 2006) that correlate axial ligand identity with physicochemical properties and antibacterial response are still relatively scarce. This gap limits the development of structure–property relationships necessary for rational design of functional cobalt(III) macrocyclic systems.

The axial ligands (NO_3^-, NO_2^-, SCN^-, Br^-, and I^-) selected in the present study were chosen to provide a diverse range of donor atoms (O-, N-, S- and X-based donors; where X= Cl, Br, or I), ligand field strengths, and polarizabilities. These ligands also differ significantly in size, coordinating ability, and electronic properties, allowing systematic evaluation of steric and electronic influences on cobalt(III) coordination behavior. Furthermore, several of these anions are known to affect lipophilicity and membrane interaction characteristics, making them particularly relevant for assessing variations in antibacterial activity among structurally related complexes.

Characterization of various six-coordinate cobalt(III) complexes of Me_8[14]diene (Roy et al., 2006) have been reported in the present work. The trans-dichlorido cobalt(III) precursor was prepared via aerial oxidation and subsequently subjected to axial substitution reactions with NO_3^-, NO_2^-, SCN^-, Br^-, and I^- ions. Structural and electronic features were elucidated using CNH analysis, Electrolytic conductance, infrared and NMR spectroscopy, magnetic susceptibility measurements, and electronic spectral studies. Antibacterial activities were evaluated to establish correlations between axial ligand identity, coordination environment, and biological response. This study provides mechanistic insight into axial ligand effects in sterically constrained cobalt(III) macrocyclic systems and contributes to the development of structure–property relationships relevant to both coordination chemistry and antimicrobial applications.

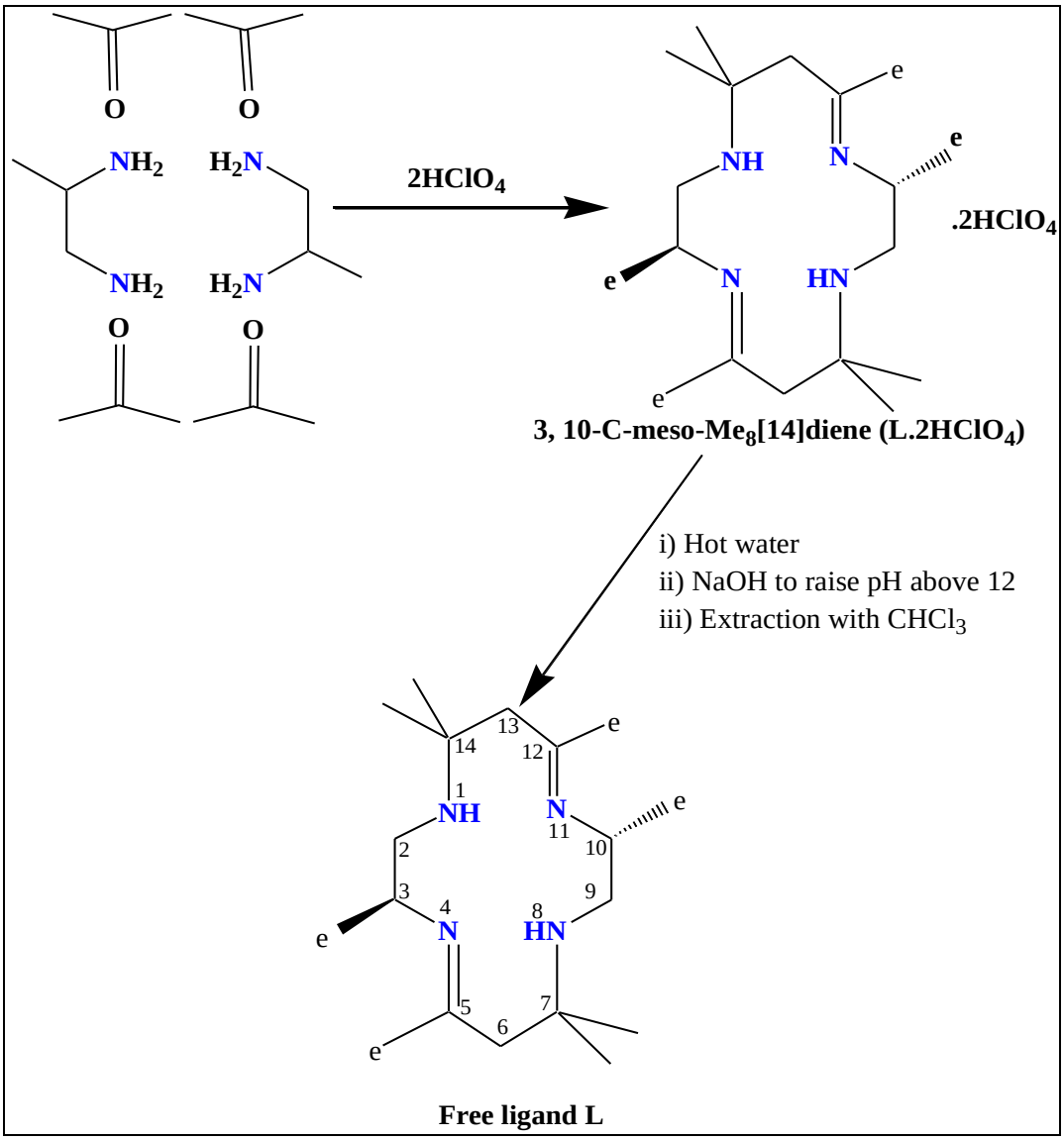
Experimental

Materials and reagents

All the chemicals and solvents used in this experiment were analytical grade quality and used as such unless mentioned otherwise. Cobalt(II) acetate tetrahydrate, KNO_3, KSCN, $NaNO_2$, KBr, KI, methanol, ethanol, chloroform, diethyl ether, hydrochloric acid, and perchloric acid were obtained from commercial sources.

Ligands

The macrocyclic ligand salt Me_8[14]diene·2$HClO_4$ (L·2$HClO_4$) (Roy et al., 2006) was synthesized as per literature procedure (Curtis et al., 1969). The free ligand L was isolated from its perchlorate salt following our reported method (Rabi et al., 2022) (Scheme 1).



Scheme 1. Synthesis of free ligand L

Synthesis of Cobalt(III) complexes

Synthesis of *trans*-$[CoL_{\alpha}Cl_2](ClO_4)$ and *trans*-$[CoL_{\beta}Cl_2](ClO_4)$

Cobalt(II) acetate tetrahydrate (0.25 g, 1.0 mmol) along with ligand L (0.308 g, 1.0 mmol) was dissolved in chilled methanol (40 mL). During the process of bubbling air into the solution for 4 hours, the color turned brown, indicating oxidation to Co(III). Concentrated HCl (2–3 drops) was added, producing a deep green solution. Heating took place on a water bath until the volume became 15 mL. On cooling of this solution, a few drops of $HClO_4$ were cautiously added, followed by reheating. The immediate formation of green color precipitate was noticed. On allowing the mixture to stand for 30 minutes, the solid was filtered out using methanol as wash until acid free, followed by ethanol and ether, to give trans-$[CoL_{\alpha}Cl_2](ClO_4)$. On standing, a second green precipitate separated from the filtrate and was collected similarly to give *trans*-$[CoL_{\beta}Cl_2](ClO_4)$.

Caution: Since the perchlorates are explosive in nature so the melting points of the compounds were not measured, moreover during syntheses, reactions were carried out in water bath at low temperature avoiding exposure to heat.

For *trans*-$[CoL_{\alpha}Cl_2](ClO_4)$: Yield: 72%. (536.04); Color, Green. Anal. Calcd (%): C, 40.29; H, 6.90; N, 10.44. Found: C, 40.27; H, 6.85; N, 10.40. IR (KBr disc, cm^{-1}): ν(N–H), 3204m; ν(C–H), 2981w; ν(CH_3), 1378m; ν(C–C),1166w; ν(C=N),1648; ν(ClO_4^-), 1092w and 623vs. Electrolytic conductance ($ohm^{-1}\,cm^2mol^{-1}$) in DMSO, 80; in acetonitrile, 153; in Chloroform 121.. ^{1}H NMR (400 MHz, DMSO, 25°C, TMS): For CH_3, δ 1.197 (s, a, 6H), 1.627 (s, e, 6H), 1.357 (d, a, 3H), 1.460 (d, e, 3H), 2.619 (s, e, 6H). For CH_2 & NH, δ 1.231 (s, 2H), 1.536 (s, 2H), 2.718 (m), 2.993 (m), 3.202 (m), 4. 401 (m), 4.5591 (m). Magnetic moment μ_{eff} (BM): Diamagnetic. UV vis [λ_{max} in nm (ε_{max})] in DMSO: 364(3777), 631(54); in CH_3CN, 302(3990), 630(55); in $CHCl_3$, 223(4000), 285(4000), 323(4000), 624(58).

For *trans*-$[CoL_{\beta}Cl_2](ClO_4)$: Yield: 44%. (536.04); Color, Green. Anal. Calcd (%): C, 40.29; H, 6.90; N, 10.44. Found: C, 40.26; H, 6.95; N, 10.33. IR (KBr disc, cm^{-1}): ν(N–H), 3198 m; ν(C–H), 2983w; ν(CH_3), 1383m; ν(C–C), 1192w; ν(C=N), 1653; ν(ClO_4^-), 1120w and 624vs. Electrolytic conductance ($ohm^{-1}cm^2mol^{-1}$) in DMSO, 130; in Acetonitrile, 155; in chloroform 56. ^{1}H-NMR (400 MHz, DMSO, 25°C, TMS): For CH_3, δ 1.334 (os, a, 6H), 1.625 (s, e, 3H), 1.681 (s, e, 3H), 1.465 (d, e, 3H), 1.554(d, e, 3H), 2.623 (s, e, 6H). For CH_2 & NH, δ 1.321 (s, 2H), 1.347 (s, 2H), 3.042 (m), 3.220 (m), 3.422 (m), 4.401 (m), 4.543(m). Magnetic moment μ_{eff} (BM): Diamagnetic. UV vis [λ_{max} in nm (ε_{max})] in DMSO: 298(3884), 657(73); in CH_3CN, 635(51); in $CHCl_3$, 636(52).

Axial substitution reactions of *trans*-$[CoL_{\alpha}Cl_2](ClO_4)$: Synthesis of *trans*-$[CoL_{\alpha}(NO_3)_2](ClO_4)$

[Trans-$CoL_{\alpha}Cl_2](ClO_4)$ (0.268 g, 0.5 mmol) was dissolved in methanol (30 mL). Methanolic solution of KNO_3 (0.1011 g, 1.0 mmol) was added and the resulting mixture was heated under a steam bath. Following partial concentration, white material (KCl) was filtered off. The filtrate was heated further (15 min), then cooled, and precipitated using methanol and diethyl ether. The compound obtained was purified by dissolution in acetonitrile followed by precipitation and silica gel drying.

For *trans*-$[CoL_{\alpha}(NO_3)_2](ClO_4)$: Yield: 56%. (589.01); Color, Dark Green. Anal. Calcd (%): C, 36.67; H, 6.28; N, 14.24. Found: C, 36.58; H, 6.19; N, 14.15. IR (KBr disc, cm^{-1}): ν(N–H), 3204w; ν(C–H), 2980w; ν(CH_3), 1383vs; ν(C–C), 1166vs; (C=N), 1646s; ν(NO_3), 1448s; ν(ClO_4^-), 1093s and 623vs . Electrolytic conductance ($ohm^{-1}cm^2mol^{-1}$) in DMSO, 120; in acetonitrile, 159. Magnetic moment μ_{eff} (BM): Diamagnetic. UV vis [λ_{max} in nm (ε_{max})] in DMSO: 212(-3230), 232(-2857), 258(4000), 277(4000), 312(4000), 337(4000), 628(173); in CH_3CN, 225(4000), 270(4000), 332(2140), 590(67), 651(69).

Other axially substituted complexes, *trans*-[$CoL_\alpha(SCN)_2$](ClO_4), *trans*-[$CoL_\alpha(SCN)_2$](SCN), *trans*-[$CoL_\alpha(ONO)_2$](ClO_4), *trans*-[$CoL_\alpha Br_2$](ClO_4), *trans*- [$CoL_\alpha I_2$](ClO_4) and *trans*-[$CoL_\alpha I_2$]I

The complexes *trans*-[$CoL_\alpha(SCN)_2$](ClO_4), *trans*-[$CoL_\alpha(SCN)_2$](SCN), *trans*-[$CoL_\alpha(ONO)_2$](ClO_4), *trans*-[$CoL_\alpha Br_2$](ClO_4), *trans*-[$CoL_\alpha I_2$](ClO_4) and *trans*-[$CoL_\alpha I_2$]I were synthesized analogously by treating *trans*-[$CoL_\alpha Cl_2$](ClO_4) with the appropriate potassium or sodium salts (KSCN, $NaNO_2$, KBr, KI) in methanol under similar conditions.

For *trans*-[$CoL_\alpha(ONO)_2$](ClO_4): Yield: 54%. (559.01); Color, Orange. Anal. Calcd (%): C, 38.63; H, 6.62; N, 15.02. Found: C, 38.64; H, 6.69; N, 15.08. IR(KBr disc, cm^{-1}): ν(N–H), 3159w; ν(C–H), 2967m; (CH_3), 1383m; ν(C–C), 1178w; ν(C=N), 1643; ν(N=O), 1427 m; ν(ClO_4^-), 1089w and 621vs. Electrolytic conductance ($ohm^{-1}cm^2mol^{-1}$) in DMSO, 128; in acetonitrile, 133; in Chloroform 121; in Water 73. ^{13}C-NMR (100.6 MHz, DMSO, 25°C, TMS): For peripheral carbons: δ 19.043, 19.114, 19.387, 20.559, 21.041, 27.111, 28.049, 28.532. For ring carbons other than sp^2 carbons: δ(ppm) = 54.644, 55.089, 55.295, 56.371, 56.736, 57.003, 60.937, 61.114. For sp^2 carbons: δ 186.053, 187.358. Magnetic moment μ_{eff} (BM): Diamagnetic. UV vis [λ_{max} in nm (ε_{max})]: in DMSO, 234(-952), 264(4000), 287(4000), 315(4000), 361(4000); in $CHCl_3$, 226(4000), 293(4000), 353(1755), 792(4); in CH_3CN, 252(4000), 271(4000), 289(4000), 306(4000); in H_2O, 242(3934), 472(138).

For *trans*-[$CoL_\alpha(SCN)_2$](ClO_4): Yield: 57%. (583.01); Color, Greyish Pink. Anal. Calcd (%): C, 41.17; H, 6.34; N, 14.75. Found: C, 41.04; H, 6.37; N, 14.53. IR (KBr disc, cm^{-1}): ν(N–H), 3232vw; ν(C–H), 2976w; ν(CH_3), 1382m; ν(C=N), 1648m, (CN), 2100, ν(CS), 798vw; δ(NCS), 469vw; ν(ClO_4^-), 1122m and 624w. Electrolytic conductance (ohm^{-1} cm^2mol^{-1}) in DMSO, 96; in Acetonitrile 131. Magnetic moment μ_{eff} (BM): Diamagnetic. . UV vis [λ_{max} in nm (ε_{max})] in DMSO: 240(1091), 278(4000), 337(4000), 350(4000), 363(4000), 542(189); in CH_3CN, 248(4000), 554(285).

For *trans*-[$CoL_\alpha(SCN)_2$](SCN): Yield: 60%. (541.50); Color, Greyish Pink. Anal. Calcd (%): C, 44.32; H, 6.84; N, 15.88. Found: C, 44.16; H, 6.76; N, 15.67. IR (KBr disc, cm^{-1}): ν(N–H), 3235w; ν(C–H), 2928vw; ν(CH_3), 1383s; ν(C–C), 1182vw; ν(C=N), 1650m; ν(CN), 2106, ν(CS), 796vw; δ(NCS), 471vw. Electrolytic conductance (ohm^{-1} cm^2mol^{-1}) in DMSO, 175; in Acetonitrile 125, in Water 162. Magnetic moment μ_{eff} (BM): Diamagnetic. UV vis [λ_{max} in nm (ε_{max})] in DMSO, 279(4000), 536(169); in CH_3CN, 231(4000), 260(4000), 360(2780), 551(202). in H_2O, 248(4000), 310(3086), 351(3856), 527(202).

For *trans*-[$CoL_\alpha(Br)_2$](ClO_4): Yield: 62%. (626.81); Color, Lemon Green. Anal. Calcd (%): C, 34.46; H, 5.90; N, 8.93. Found: C, 34.51; H, 5.85; N, 8.95. IR (KBr disc, cm^{-1}): ν(N–H), 3200w; ν(C–H), 2981w; ν(CH_3), 1383s; ν(C–C), 1166w; ν(C=N), 1647m; ν(ClO_4^-), 1092vs and 622m. Electrolytic conductance ($ohm^{-1}cm^2mol^{-1}$) in DMSO, 22. Magnetic moment μ_{eff} (BM): Diamagnetic. UV vis [λ_{max} in nm (ε_{max})] in DMSO, 194(-3619) 226(-2857), 258(4000), 286(4000), 328(4000), 634(179); in CH_3CN, 222(4000), 295(4000), 346(4000), 696(121); in $CHCl_3$, 232(4000), 267(4000), 321(4000).

For *trans*-[$CoL_\alpha(I)_2$](ClO_4): Yield: 36%. (720.81); Color, Light Brown. Anal. Calcd (%): C, 29.96; H, 5.13; N, 7.77. Found: C, 29.89; H, 5.16; N, 7.61. IR (KBr disc, cm^{-1}): ν(N–H), 3199w; ν(C–H), 2932w; (CH_3), 1383vs; ν(C–C), 1230w; ν(C=N), 1650m; ν(ClO_4^-), 1120m and 625s. Electrolytic conductance ($ohm^{-1}cm^2mol^{-1}$) in DMSO, 123; in Acetonitrile, 109; in Chloroform 78. Magnetic moment μ_{eff} (BM): Diamagnetic. UV vis [λ_{max} in nm (ε_{max})] in DMSO: 212(-3230), 232(-2857), 258(4000), 277(4000), 312(4000), 337(4000), 628(173); in CH3CN, 225(4000), 270(4000), 332(2140), 590(67), 651(69). UV vis [λ_{max} in nm (ε_{max})] in DMSO, 400(4000), 233(1091), 241(-3273), 313(4000), 384(4000), 391(4000); in CH_3CN, 301(4000), 325(4000), 353(4000), 400(4000); in $CHCl_3$, 296(4000).

For *trans*-[$CoL_\alpha(I)_2$]I: Yield: 44%. (720.81); Color, Dark Brown. Anal. Calcd (%): C, 28.87; H, 4.94; N,

7.48. Found: C, 28.78; H, 4.86; N, 7.57. IR (KBr disc, cm^{-1}): ν(N–H), 3024vw; ν(C–H), 2924w; ν(CH_3), 1383vs; ν(C–C), 1141w; ν(C=N), 1651m. Electrolytic conductance ($ohm^{-1}cm^2mol^{-1}$) in DMSO, 112; in Acetonitrile, 125; in Chloroform 54. Magnetic moment μ_{eff} (BM): Diamagnetic. UV vis [λ_{max} in nm (ε_{max})] in DMSO, 255(320000, 271(16400), 306(32000), 358(11888), 391(4000); in CH_3CN, 263(4324) 328(2072) 357(3284); in $CHCl_3$, 260(9570), 340(40000), 598(690).

Physical measurement

CHN analysis was done by means of LECO CHNS-932 elemental analyzer (C, H, N). Infrared spectra were acquired using Shimadzu IR-20 spectrophotometer with KBr pellet technique in the region 4000-400 cm^{-1}. The ^1H and ^{13}C NMR spectra were acquired using Bruker AVANCE 400 MHz spectrometer using DMSO-d6 as solvent and TMS as an internal standard. The molar conductance values were determined using Hanna HI-8820 Conductivity Bridge at ambient temperature. Magnetic behavior (μ_{eff}) was measured at room temperature.

Antibacterial studies

The antibacterial effects of the prepared cobalt(III) complexes on selected strains of bacteria were investigated following established procedures reported elsewhere (Alam et al., 2018). Experimental parameters, culture media, and experimental methodology were kept identical to what has been reported in our previous work.

Results and Discussion

All the synthesized cobalt(III) complexes are different in color because of the axial ligand effect. They have been characterized with the help of elemental analysis, conductivity studies, IR, NMR spectroscopy, electronic spectrophotometry, and magnetic susceptibility studies as follows. All the complexes are diamagnetic in nature, which is expected from a low spin d^6 complex. The stereochemistry of the trans-dichlorido cobalt(III) complexes has been determined with the help of the ^1H-NMR study of the complexes. However, the stereochemistry of the axial substitution complexes is known from the fact that axial substitution does not affect the conformation and configuration of the ligand (Roy et al., 2006).

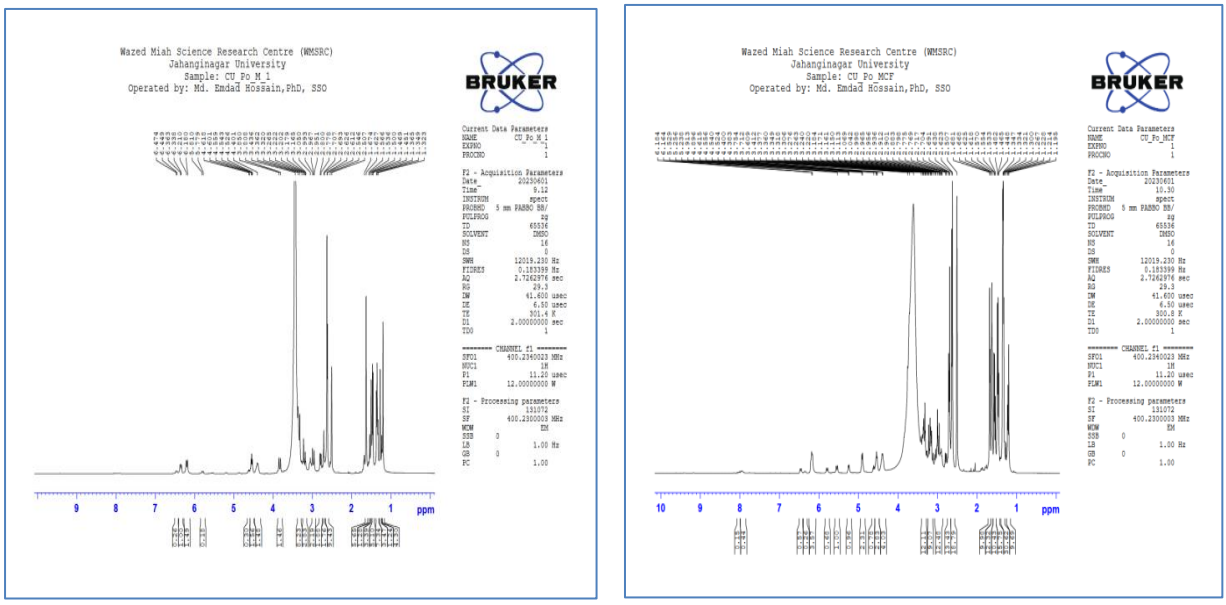


Fig. 1. ^1H-NMR spectra of *trans*-$[CoL_\alpha Cl_2](ClO_4)$ (left) and *trans*-$[CoL_\beta Cl_2](ClO_4)$ (right).

However, characterization of the ligand has been done as per earlier report [Rabi et al., 2022].

Cobalt(III) complexes *trans*-dichloridocobalt-(III) complexes, *trans*-[CoL*α*Cl_2](ClO_4) and *trans*-[$CoL_\beta Cl_2$](ClO_4)

The IR spectra of the diastereomeric cobalt(III) complexes, *trans*-[$CoL_\alpha Cl_2$](ClO_4) and *trans*-[$CoL_\beta Cl_2$](ClO_4) exhibit intense ClO_4^- bands at 1092-1120 cm^{-1} and 619-624 cm^{-1}, $\nu_{C=N}$ at 1602-1657 cm^{-1}. An stretching vibration of the Co–Cl band in the IR region between 250-300 cm^{-1} could not be observed since the IR spectrum could not be carried out below 400 cm-1. Position and absence of splitting of bands near 1100 cm^{-1} provide convincing evidence that ClO_4^- is not coordinated in the complex. The other bands appearing at 2981-2983, 1166-1192 and 517-562 cm^{-1} are attributed to C-H, C-C and Co-N stretching frequencies respectively. Appearance of the bands at 1374-1383 cm^{-1} are the indication of presence of CH_3 groups. The difference in the splitting of bands in the region of 700-950 cm^{-1} in these two fractions indicates that they are diasteriomers. The conductance values of 80 and 121 ohm^{-1} cm^2 mol^{-1} in DMSO and chloroform respectively for trans-[$CoL_\alpha Cl_2$](ClO_4) and 130 & 56 $ohm^{-1}cm^2mol^{-1}$ in the same solvents for *trans*-[$CoL_\beta Cl_2$](ClO_4) matching to 1:1 electrolytes support (Geary, 1971) the six coordinated complexes of cobalt(III) as expected for the molecular formulae *trans*-[$CoL_\alpha Cl_2$](ClO_4) and *trans*-[$CoL_\beta Cl_2$](ClO_4).

However, the values of 153 and 155 $ohm^{-1}cm^2mol^{-1}$ in acetonitrile for *trans*-[$CoL_\alpha Cl_2$](ClO_4) and *trans*-[$CoL_\beta Cl_2$](ClO_4) respectively corresponding to 1:2 electrolytes can be accounted for the following conversion-1.

$$[CoL'Cl_2](ClO_4) \xrightarrow{\mathbf{CH_3CN}} [CoL'Cl(CH_3CN)](Cl)(ClO_4)$$

($L' = L_\alpha$ or L_β) (1)

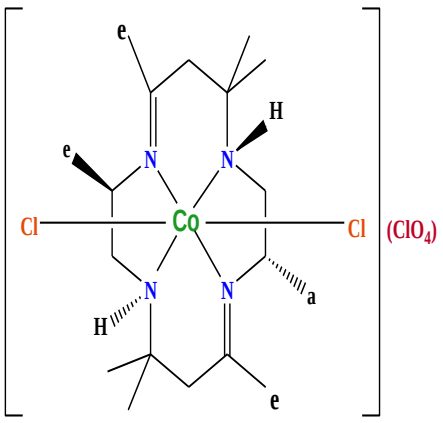
The magnetic properties of the complex *trans*-[$CoL_\alpha Cl_2$](ClO_4) and *trans*-[$CoL_\beta Cl_2$](ClO_4) are in good agreement with diamagnetic cobalt(III) complexes having all d electrons in their d^6 system. In this case, the electronic spectra of these complexes show d-d transition bands at wavelengths 624-657 nm in DMSO and chloroform which is expected in case of a CoN_4Cl_2 chromophore. In particular, the wavelengths of these bands are comparable very well with that reported for the other related cobalt(III) macrocycles (Roy et al., 2006; Hay et al., 1977). These bands suggest that there is a trans configuration around the two coordinated chloride ions. However, in addition to the above bands, other bands have been observed at wavelengths 298-364 nm in DMSO, 223-323 nm, in chloroform, and 302 nm in acetonitrile with high extinction coefficients in the UV region.

The ^{1}H-NMR of *trans*-[$CoL_\alpha Cl_2$](ClO_4) exhibits two doublets and four singlets in the region of 1.197-2.674 ppm. This region is accounted for peripheral methyl and β methylene groups. The total integration of these signals corresponds to 28 protons. The singlets at 1.197 and 1.627 ppm each corresponding to 6H can be accounted for axial and equatorial components of gem-dimethyl pairs. The other two singlets at 1.231 and 1.536 ppm each corresponding to 2H can be assigned to two β-CH_2 protons. However, the two doublets at 1.357 and 1.460 each corresponding to 3H can be assigned to axial and equatorial methyls respectively on chiral carbons. The downfield singlet at 2.619 ppm due to 6H can be attributed to two equatorial methyls on two sp^2 carbons. Other down fielded multiplets at 2.718, 2.993, 3.202, 4.559 and 4.401 ppm etc. can be accounted for other CH_2, CH and NH protons. Thus an axial-equatorial orientation can be assigned to *trans*-[$CoL_\alpha Cl_2$](ClO_4). In contrast, the ^{1}H-NMR spectrum of *trans*-[$CoL_\beta Cl_2$](ClO_4) displays one overlapped signal at 1.334 ppm consisting of three singlets with a total integration of 10H. One singlet of 6H corresponds to axial components of gem-dimethyl pairs. Other two at 1.321 and 1.347 ppm, each of 2H correspond to two β-CH_2 protons. The

spectrum exhibits two more singlets at 1.625 and 1.681 ppm each of 3H which can be assigned two equatorial methyl of gem-dimethyl pair. Two sets of doublets at 1.465 ppm and 1.554 ppm of 3H can be explained due to equatorial orientation of methyl protons attached to two sp^2 hybridized carbons. The downshifted multiplets at 3.042 ppm, 3.220 ppm, 3.422 ppm, 4.401 ppm and 4.543 ppm can be accounted for other CH_2, CH and NH protons. So, a diequatorial orientation can be assigned to the ligand structure of *trans*-$[CoL_\beta Cl_2](ClO_4)$. Thus on the basis of all evidences, the structure Str.-1 and Str.-2 can be accounted for *trans*-$[CoL_\alpha Cl_2](ClO_4)$ and *trans*-$[CoL_\beta Cl_2](ClO_4)$ respectively.

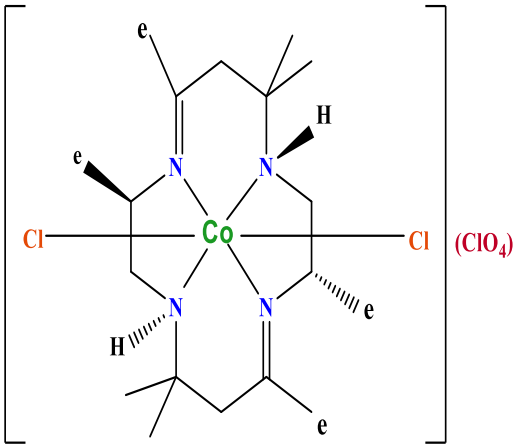
Axial substitution products of *trans*-$[CoL_\alpha Cl_2](ClO_4)$

trans-dichloridocobalt(III) complex, *trans*-$[CoL_\alpha Cl_2](ClO_4)$, readily undergoes axial ligand substitution reactions with small unidentate ligands like SCN^-, NO_2^-, NO_3^-, I^- and Br^- in the ratio of 1:2 to result in corresponding six-coordinated trans derivatives. IR of them show ν_{NH}, ν_{C-H}, ν_{C-C}, $\nu_{C=N}$ and ν_{CH3} bands at 3024–3235, 2924–2981, 1141–1230, 1643-1651 and 1382-1383 cm^{-1} respectively. Moreover these complexes except



Str. -1

trans-$[CoL_\alpha(SCN)_2](SCN)$ and trans-$[CoL_\alpha(I)_2](I)$ display ν_{ClO4^-} at 1089-1122 and 621-624 cm^{-1}. Presence of ν_{N-Co} band at 584 cm^{-1} and $\nu_{N=O}$ and υ_{NO} bands at 1427 cm^{-1} and 1080 cm^{-1} overlapped with ClO_4^- band in the IR spectrum of *trans*-$[CoL_\alpha(ONO)_2](ClO_4)$ support the complex to be O-bonded nitrito complex (Nakamoto, 1986). Once again in the case of trans-$[CoL\alpha(NO_3)_2](ClO_4)$, the absorption at 1383 cm^{-1} signifies that there is νNO_3 band along with νCH_3 band while the splitting of this band at 1323 and 1437 cm^{-1} with a difference of 114 cm^{-1} shows that NO^{3-} ions coordinate in an unidentate fashion (Curtis & Curtis, 1965). Moreover, *trans*-$[CoL_\alpha(SCN)_2](ClO_4)$ and *trans*-$[CoL_\alpha(SCN)_2](SCN)$ display bands at 2100-2106 cm-1 796-798 cm^{-1} and some bands of low intensities at around 420 cm^{-1} which indicates the presence of ν_{CN}, ν_{CS}, δ_{NCS} bands respectively. Such vibrations do not belong to any band of the ligand in the region under consideration, and hence they are associated with the fully S-bonded thiocyanate group (Farago and James, 1965; Sabatini and Bertin, 1965). Consequently, both compounds can be characterized as S-bonded thiocyanato complexes (Sabatini and Bertin, 1965). As the spectrum was not obtained below 400 cm-1, it was not possible to record the Co-Cl/Br/I vibrations at about 260 cm^{-1} in the halo compounds.



Str.-2

The conductance values 54-133 $ohm^{-1}cm^2mol^{-1}$ of these complexes in DMSO, acetonitrile, water and chloroform correspond to 1:1 electrolytes except few cases like conductivity values of 159-175 ohm-

$^{1}cm^{2}mol^{-1}$ for the complexes *trans*-$[CoL_{\alpha}(NO_3)_2]ClO_4$ and trans-$[CoL_{\alpha}(SCN)_2](SCN)$, and 22 $ohm^{-1}cm^{2}mol^{-1}$ in water for *trans*-$[CoL_{\alpha}Br_2](ClO_4)$. This observation indicates that one anion, like ClO_4-/SCN/I is out of the coordination sphere, which supports the six-coordinated complex of cobalt(III) as expected for molecular formulae assigned. However, the conductance value 159 $ohm^{-1}cm^{2}mol^{-1}$ of $[CoL_{\alpha}(NO_3)_2](ClO_4)$ in CH_3CN corresponding to 1:2 electrolytes can be accounted for by the Expression-2 given below.

$$[CoL_{\alpha}(NO_3)_2](ClO_4) \xrightarrow{CH_3CN} [CoL_{\alpha}(NO_3)(CH_3CN)](NO_3)(ClO_4) \quad (2)$$

Similarly the values of 175, and 162 $ohm^{-1}cm^{2}mol^{-1}$ of the complex $[CoL_{\alpha}(SCN)_2](SCN)$ in DMSO and water respectively corresponding to 1:2 electrolytes [Geary, 1971] can be accounted for the expression-3

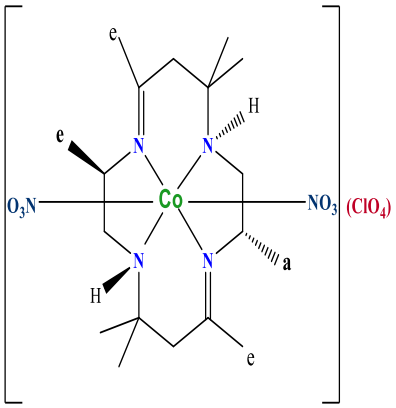
$$[CoL_{\alpha}(SCN)_2](SCN) \xrightarrow{DMSO/H_2O} [CoL_{\alpha}(SCN)(DMSO/H_2O)](SCN)_2 \quad (3)$$

Moreover the conductance value 22 ohm^{-1} cm^{2} mol^{-1} of *trans*-$[CoL\alpha(Br)_2](ClO_4)$ in water is an indication of anion association rather than increase of coordination number of cobalt(III) (Nath et al., 2018).

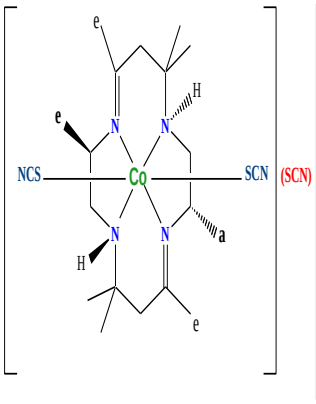
The number of ^{13}C-NMR signals observed for *trans*-$[CoL_{\alpha}(ONO)_2](ClO_4)$ corresponds to number of nonequivalent carbon atoms. The assignments have been done based on the literature study (Muralidhar et al., 2007). The peaks between the region of 19-28 have been considered to assign to peripheral carbons whereas those between the region of 54-62 ppm have been considered to assign to ring carbons except sp^2 carbons. In this case, the peaks at 186.053 ppm and 187.358 ppm have been considered to assign to sp^2 carbons. This results in total 18 peaks for 18 non-equivalent carbons as expected for less symmetrical axial-equatorial orientation (based on the fact mentioned in earlier section 3). The electronic spectra of these complexes feature *d–d* bands at 536-634 nm in DMSO, 598-798 nm in chloroform, 400-651 nm in acetonitrile and 472-527 nm in water, which are in good agreement with those of six-coordinate octahedral cobalt(III) complexes (Roy et al., 2006; Hay et al., 1977). These bands can be attributed to the $^{1}A_{1g}\rightarrow{}^{1}T_{1g}$ transition, in which case the tetragonal splitting will be small (Hay et al., 1977). The other bands ranging between 328-384 nm with high extinction in UV spectrum can be attributed to the charge transfer transition. From the above discussion, we can assign the following structures, Str.-3, Str.-4, Str.-5, Str.-6, Str.-7, Str.-8, and Str.-9 to the axial substituted compounds, *trans*-$[CoL_{\alpha}(SCN)_2](ClO_4)$, *trans*-$[CoL_{\alpha}(SCN)_2](SCN)$, *trans*-$[CoL_{\alpha}(ONO)_2](ClO_4)$, *trans*-$[CoL_{\alpha}Br_2](ClO_4)$, *trans*-$[CoL_{\alpha}I_2](ClO_4)$ and *trans*-$[CoL_{\alpha}I_2]I$ respectively of the mother complex *trans*-$[CoL_{\alpha}Cl_2](ClO_4)$.

Antibacterial activities

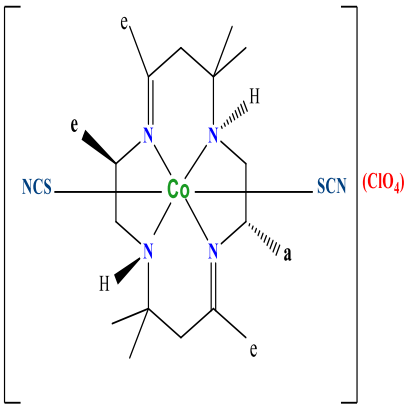
The ligand salt, $L{\cdot}2HClO_4$ as well as in free state (L) did not reveal any activity but the concerned cobalt(III) complexes exhibit different activity against different bacteria. All tested compounds demonstrated remarkable activity against *Bacillus subtillis and E. coli* but *trans*-$[CoL_{\alpha}(SCN)_2](ClO_4)$ was the most potent among them against *B. subtilis*. Again, all the complexes show good activity against *B. cereus* where trans-$[CoL_{\alpha}Br_2](ClO_4)$ was the most potent one. In case of *S. typhi* and *V. cholera*, trans-$[CoL\alpha Cl_2](ClO_4)$ and *trans*- $[CoL_{\beta}Cl_2](ClO_4)$ exhibit highest antibacterial activity respectively. However some complexes showed ineffectiveness against some bacteria but a minute comparison on the result (Table-1) reveals that *trans*-$[CoL_{\alpha}Cl_2](ClO_4)$, *trans*-$[CoL_{\beta}Cl_2](ClO_4)$, *trans*-$[CoL_{\alpha}(NO_3)_2](ClO_4)$, *trans*-$[CoL\alpha(ONO)2](ClO4)$, and *trans*-$[CoL_{\alpha}(NCS)_2](ClO_4)$, *trans*-$[CoL_{\alpha}(NCS)_2](SCN)$, showed activity against all bacteria.



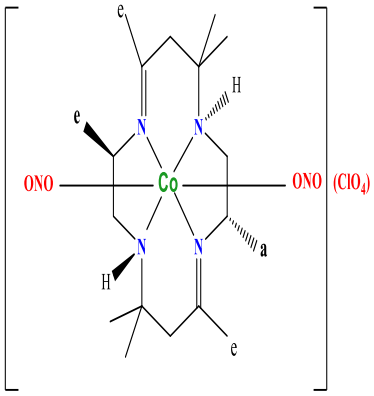
Str-3



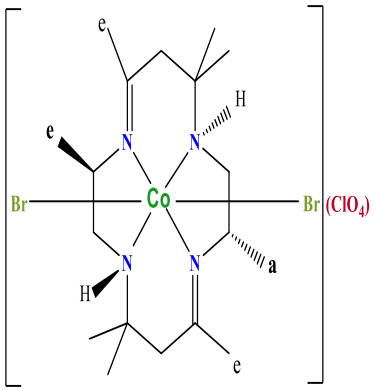
Str-4



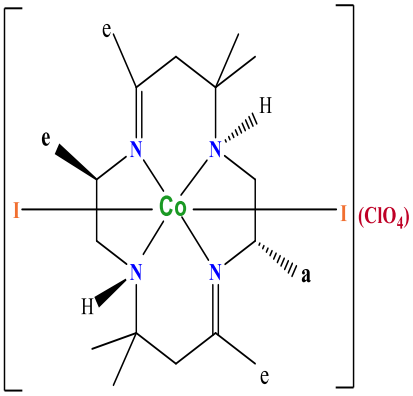
Str-5



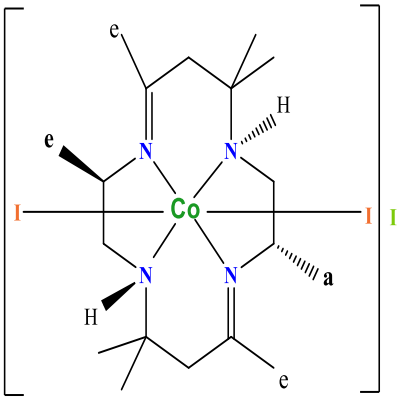
Str-6



Str-7



Str-8



Str-9

Table 1. Antibacterial activities.

Test compounds	Diameter of zone of inhibition (mm)				
	Gram-positive		Gram-negative		
	B. cereus	*B. subtilis*	*S. typhi*	*V. Cholera*	*E. coli*
	24 h incubation				
trans-$[CoL_{\alpha}Cl_2](ClO_4)$	7	14	12	9	12
trans- $[CoL_{\beta}Cl_2](ClO_4)$	9	12	8	11	12
trans-$[CoL_{\alpha}(ONO)_2](ClO_4)$	9	14	7	10	11
trans-$[CoL_{\alpha}(NO_3)_2](ClO_4)$	9	15	9	8	11
trans-$[CoL_{\alpha}(NCS)_2](ClO_4)$	8	16	10	9	12
trans- $[CoL_{\alpha}(NCS)_2](SCN)$	8	12	8	9	10
trans-$[CoL_{\alpha}Br_2](ClO_4)$	10	11	0	0	10
trans- $[CoL_{\alpha}I_2](ClO_4)$	8	15	0	0	12
trans- $[CoL_{\alpha}I_2]I$	8	15	0	8	11
DMSO	0	0	0	0	0
Ampicillin	26	24	30	32	32

Conclusion

This study reveals that the concerned isolated free ligand 'L' undergoes facile complexation when aerated with cobalt(II) acetate tetrahydrate, $Co(OAC)_2.4H_2O$ followed by addition of HCl and $HClO_4$. The reaction is found to produce six coordinated diastereoiomeric cobalt(III) octahedral complexes, *trans*-$[CoL_{\alpha}Cl_2](ClO_4)$ and *trans*-$[CoL_{\beta}Cl_2](ClO_4)$. The diastereoisomeric trans-dichloridocobalt(III) complex, *trans*-$[CoL_{\alpha}Cl_2]$ (ClO_4) readily undergoes axial ligand substitution reactions with small unidentate ligands like SCN^-, NO_2^-, NO_3^-, I^- and Br^- to form corresponding *trans*- derivatives.

The complexes are diamagnetic in nature as expected. The conductance values in different solvents corresponding to 1:1 electrolytes indicates that one anion is out of coordination sphere as expected. Since this macrocyclic ligand is sterically congested with eight peripheral methyl groups, it was doubtful whether this complex will undergo axial substitution reactions or not, but practically this complex did so as like the complexes of other di-, tri-, tetra- and penta-methyl substituted macrocycles. It should be noted that, in biological studies, many complexes have been discovered to

possess the ability to act as antibacterial compounds, but there are some complexes which do not work on certain bacteria.

Authors contribution

Puja Chakraborty and Manisha Rani Roy have drafted the manuscript and performed the experiments. Saswata Rabi has been analyzed and interpreted the data. Suman Kanti Das Gupta and Debashis Palit contributed reagents, materials, analysis tools and also edited the manuscript. Tapashi Ghosh Roy did the conception and design of the study, analyzed and interpreted the data, critically revised the important intellectual content, and finally maintained the total submission process of the manuscript.

Conflict of interest

The authors declare that they have no conflicts of interest regarding the publication of this article.

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