Oxygen atom transfer promoted nitrate to nitric oxide transformation: a step-wise reduction of nitrate → nitrite → nitric oxide†

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Nitrate reductases (NRs) are molybdoenzymes that reduce nitrate (NO$_3^-$) to nitrite (NO$_2^-$) in both mammals and plants. In mammals, the salivary microbes take part in the generation of the NO$_3^-$ from NO$_2^-$, which further produces nitric oxide (NO) either in acid-induced NO$_2^-$ reduction or in the presence of nitrite reductases (NiRs). Here, we report a new approach of VCl$_3$ (V$^{V+}$ ion source) induced step-wise reduction of NO$_3^-$ in a Co$^{II}$-nitrato complex, ([12-TMC]Co$^0$(NO$_3$))$^+$ (2,[Co$^{II}$-NO$_3$])$_2$ to a Co$^{III}$-nitrosyl complex, [[12-TMC]Co$^0$(NO)]$^{2+}$ (4,[CoNO])$_2$, bearing an N-tetramethylene cyclam (TMC) ligand. The VCl$_3$ inspired reduction of NO$_3^-$ to NO is believed to occur in two consecutive oxygen atom transfer (OAT) reactions, i.e., OAT-1 = NO$_3^-$ → NO$_2^-$ (r$_1$) and OAT-2 = NO$_2^-$ → NO (r$_2$). In these OAT reactions, VCl$_3$ functions as an O-atom abstracting species, and the reaction of 2 with VCl$_3$ produces a Co$^{III}$-nitrosyl ([CoNO])$_2$, hence the reaction moves in the forward direction (OAT-1). However, K$_{\text{BiCo}^{O^{III}}\text{NO}_3}$ is higher than K$_{\text{BiCo}^{O^{II}}\text{NO}_2}$, hence the reaction moves in the forward direction (OAT-1). However, K$_{\text{BiCo}^{O^{III}}\text{NO}_3}$ is comparable to K$_{\text{BiCo}^{O^{II}}\text{NO}_3}$, and therefore sequenced the second OAT reaction (OAT-2). Mechanistic investigations of these reactions using $^{15}$N-labeled-15NO$_3^-$ and $^{15}$NO$_2^-$ revealed that the N-atom in the (CoNO)$_2$ is derived from NO$_3^-$ ligand. This work highlights the first-ever report of VCl$_3$ induced step-wise NO$_3^-$ reduction (NRs activity) followed by the OAT induced NO$_2^-$ reduction and then the generation of Co-nitrosyl species (CoNO)$_2$.

Introduction

The mechanism of microbial denitrification is still one of the most mysterious subjects, despite being explored in detail in both in vivo and in vitro systems. Based on the extensive research and literature available, denitrification has been well accepted to be a four-step reductive process of nitrate (NO$_3^-$) to dinitrogen (N$_2$) conversion [NO$_3^-$ → NO$_2^-$ → NO → N$_2$O → N$_2$], through a series of intermediate gaseous nitrogen oxide products. In mammals and bacteria, inorganic NO$_3^-$ and nitrite (NO$_2^-$) serve as a fundamental storage material of NO for its bio-physiological processes. However, in humans, an excessive amount of NO$_3^-$ has been discovered to cause gastric cancer and other disorders. To maintain an optimal NO$_3^-$ level in the bio-system, commensal bacteria in the human oral cavity play a vital role in converting NO$_3^-$ to NO$_2^-$ (eqn (1)). In bacteria, molybdenum-based nitrate reductase (NRs) enzymes generate NO$_3^{III}$ via an OAT reaction from NO$_3^-$ anion. At the bio-physiological level, NO$_3^-$ serves as a pool of NO and can easily be transformed to NO, either (i) in non-enzymatic acid-catalyzed NO$_2^-$ reduction in the stomach or (ii) by Fe and Cu based nitrite reductase (NiRs) enzymes catalyzed reactions (eqns (2)).

$$\text{NO}_3^- + \text{Mo}^{IV} \rightarrow \text{NO}_2^- + \text{Mo}^{VI}=\text{O}$$  \hspace{1cm} (1)
M–NO\textsuperscript{2−} + 2H\textsuperscript{+} + e\textsuperscript{−} → M–NO + H\textsubscript{2}O  \hspace{1cm} (2)

M–NO\textsubscript{2−} + R\textsubscript{2}S → M–NO + R\textsubscript{2}SO  \hspace{1cm} (3)

M–NO\textsubscript{2−} + RSH → M–NO + R(O)SH  \hspace{1cm} (4)

M–NO\textsubscript{2−} + PPh\textsubscript{3} → M–NO + OPPh\textsubscript{3}  \hspace{1cm} (5)

M–NO\textsubscript{2−} + Sub + h\nu → M–NO + (O)Prod  \hspace{1cm} (6)

NO is a gaseous secondary messenger in animals, plants, fungi, and bacteria. In plants, NO is involved in different physiological processes, such as plant growth & development, metabolism, aging, defense against pathogens, biotic and abiotic trauma.\textsuperscript{18} However, NO regulates various physiological processes in mammals.\textsuperscript{14} For instance, NO inadequacy possibly will aggravate the pathogenic effects associated with atherosclerosis, diabetic hypertension, etc.\textsuperscript{12} Also, the immune response of NO towards the harmful pathogens is related to the oxidized NO species,\textsuperscript{13} i.e., peroxynitrite (PN, ONOO\textsuperscript{−})\textsuperscript{13,14} or/and nitrogen dioxide ([NO\textsubscript{2}])\textsuperscript{15,16}. Hence, balanced production of NO is required to maintain a normal homeostatic bio-physiological condition. In bio-systems, enzymes, i.e., NRs\textsuperscript{9,17} and endothelial nitric oxide synthases (eNOSs)\textsuperscript{17,28} are available for NO generation. The NOS enzymes catalyze the biosynthesis of NO from L-arginine.\textsuperscript{18}

In the case of NO overproduction, nitric oxide dioxygenase (NODs) generates NO\textsubscript{3−} in the reaction of the iron–dioxogen adduct with NO via a proposed PN intermediate,\textsuperscript{19} as explored in other biomimetic systems.\textsuperscript{19a,20} Also, there are various reports on NO\textsubscript{2−} formation in nitric oxide monoxygenation (NOM) reaction from metal-nitrosyls in the presence of O\textsubscript{2}, O\textsubscript{2}− and OH\textsuperscript{−}.\textsuperscript{19a,20,21} Oxidized species of NO (NO\textsubscript{3−} & NO\textsubscript{2−}) may also generate via different oxidative processes (vide supra). However, NO\textsubscript{3−} to NO\textsubscript{2−} transformation and NO\textsubscript{2−}/NO\textsubscript{3−} to NO conversion (vise versa) are critical steps of the denitrification process.\textsuperscript{1}

In an attempt to mimic the denitrification process, R. H. Holm and co-workers reported NRs activity, molybdenum, and tungsten-based catalyst for catalytic reduction of NO\textsubscript{3−} to NO\textsubscript{2−} with metal-Oxo species.\textsuperscript{22} Similarly, S. Sarkar and co-workers have reported Mo\textsuperscript{IV} mediated reduction of NO\textsubscript{3−} to NO\textsubscript{2−} to mimic NRs activity.\textsuperscript{23} Eunsook Kim proposed the reduction of NO\textsubscript{3−} to NO\textsubscript{2−} using the Lewis acid Sc\textsuperscript{3+} to activate the OAT reaction from NO\textsubscript{3−} to Mo metal center.\textsuperscript{24} On the other hand, nitrite reduction chemistry is explored widely; Ford and co-workers examined the acid-induced reduction of NO\textsubscript{2−} to N\textsubscript{2}O in a Fe–porphyrin complex.\textsuperscript{25} Warren group described the NIR by using the thiol group.\textsuperscript{26} Recently, we have reported acid-induced nitrite reduction to NO.\textsuperscript{27} However, the conversion of NO\textsubscript{3−} to NO using a single catalyst is barely explored; Yunho Lee and co-workers testified Ni catalyzed the transformation of inorganic NO\textsubscript{3−} to N\textsubscript{2} via NO\textsubscript{2−} intermediate using the carbon monoxide (CO) as oxophilic species.\textsuperscript{28}

In biological systems,\textsuperscript{3,24} and biomimetic\textsuperscript{23,23,27,29} or catalytic reactions,\textsuperscript{24} the approach towards converting NO\textsubscript{3−} to NO is usually a two-enzymes/catalysts-induced two-step process in two different reactions (i.e., NO\textsubscript{3−} reduction followed by NO\textsubscript{2−} reduction).\textsuperscript{24} However, only a few reports simultaneously carry out both the NO\textsubscript{3−} and NO\textsubscript{2−} reduction using a single metal center in a biomimetic system. Here, our eagerness is to mimic the NRs enzymatic reaction followed by the NO\textsubscript{2−} reduction, sponsored by the same reagent (i.e., single metal-induced two-step NO\textsubscript{2−} to NO conversion). Herein, we report the NO\textsubscript{3−} reduction chemistry of a Co\textsuperscript{II}–NO\textsubscript{2−} complex, [[(12-TMC)Co\textsuperscript{III}(NO\textsubscript{3})\textsuperscript{2−}][(2, bearing a 12-TMC ligand (12-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) via the two consecutive oxygen atom transfer (OAT) reactions using VCl\textsubscript{3} as an oxophilic compound (Scheme 1, reaction II & III). Complex 2 reacts with VCl\textsubscript{3} to form corresponding Co\textsuperscript{II}-nitrosyl complex, [[(12-TMC)Co\textsuperscript{III}(NO\textsubscript{3})\textsuperscript{2−}][V\textsuperscript{V}O\textsuperscript{O} ((V\textsuperscript{V}O\textsuperscript{O})\textsuperscript{3−}) species, which further decomposes to V\textsubscript{2}O\textsubscript{5}, via the formation of a presumed Co\textsuperscript{II}–nitrato (3,[Co\textsuperscript{II}–NO\textsubscript{2−}]) intermediate in MeOH or H\textsubscript{2}O at 298 K (Scheme 1, reaction II). Interpretation of various spectral measurements, we have confirmed the generation of 3 with V\textsuperscript{V}O\textsuperscript{O} by the transfer of one O-atom from NO\textsubscript{3−} moiety of 2 to VCl\textsubscript{3} (OAT-1). Further, we observed the generation of 4 with V\textsuperscript{V}O\textsuperscript{O} from 3 upon reaction with VCl\textsubscript{3} (OAT-2), under similar reaction conditions, showing the similar OAT induced NO\textsubscript{3−} reduction reactivity as reported in the case of PPh\textsubscript{3} and sulphur based compounds (thiols and disulfides) (eqn (3)–(6)).\textsuperscript{26,22} Combining these two OAT reactions, we can predict the reaction sequences, i.e., the first OAT from NO\textsubscript{3−} moiety of 2 to VCl\textsubscript{3} and the generation of 3, \( \text{[OAT-1} = \text{Co}^{\text{II}}\text{–NO}^{\text{2−}} + \text{VCl}_3 \rightarrow \text{Co}^{\text{II}}\text{–NO}^{\text{2−}} + \text{VOCl}_\text{2} \text{]} \). Subsequently, the second OAT from NO\textsubscript{3−} moiety of 3 to another VCl\textsubscript{3} moiety and the generation of 4 \( \text{[OAT-2} = \text{Co}^{\text{II}}\text{–NO}^{\text{2−}} + \text{VCl}_3 \rightarrow \{\text{CoNO}\}^{\text{8−}} + \text{VOCl}_\text{2} \text{]} \). Mechanistic investigation using \(^{15}\text{N}\)-labeled \(^{15}\text{NO}_3\) & \(^{15}\text{NO}_2\) confirmed clearly that the N-atom in the \{CoNO\}\textsuperscript{8−} is derived from NO\textsubscript{3−} anion of 2. To the best of our knowledge, the present work reports the first example of VCl\textsubscript{3} induced conversion of Co\textsuperscript{II}–NO\textsubscript{3−} to \{CoNO\}\textsuperscript{8−} in two successive OAT reactions, demonstrating a new mechanistic approach for one-metal induced NO\textsubscript{3−} to NO\textsubscript{2−} reduction (NRs activity) followed by NO\textsubscript{2−} to NO conversion (OAT induced NO\textsubscript{2−} reduction).

\( \text{Scheme 1} \)
Results and discussion

Preparation of CoII-nitrate complex, [(12-TMC)CoII(NO3−)]+ (2) 

The primary CoII-nitrate complex, [(12-TMC)CoII(NO3−)]+ (2), was prepared by reacting CoII-complex, [(12-TMC)CoII(NCCH3)]2+ (1), with 1 equivalent of NaN3 in H2O/CH3CN (Scheme 1, the reaction I; also see ESI† and Experimental section (ES)). Further, 2 was characterized by various spectroscopic techniques, including the single-crystal X-ray structure determination. UV-vis absorption band of 1 (λmax = 485 nm) changed to a new band (λmax = 480 nm, ε = 25 M−1 cm−1) upon addition of 1 equivalent NaN3 in CH3CN at RT, suggesting the formation of 2 (Fig. 1a). FT-IR spectrum of 2 showed a characteristic peak for CoII-bound NO3− anion at 1384 cm−1 and shifted to 1358 cm−1 when exchanged with 15N-labeled-NO3− ([15N(NO3)−]−) (Fig. 1a; ESI, Fig. S1†). A wide range 1H-NMR spectrum of 2 showed fairly clean paramagnetic proton-signals (Figure S2a†), suggesting a magnetically active Co-center. The spin state of 2 was determined by calculating the magnetic moment of the CoII metal-center by the Evans’ method and found to be 4.46 BM, suggesting a high spin CoII-ion in complex 2 (ESI, S2b†). Electrospray ionization mass spectrum (ESI-MS) of 2 showed a prominent peak at m/z 349.1, which shifted to m/z 350.1 when prepared with 15N-labeled Na15NO3, and their mass and isotope distribution pattern corresponds to [(12-TMC)CoII(15NO3)]+ (calc. m/z 349.1) and [(12-TMC) CoII(15NO3)]+ (calc. m/z 350.1), respectively (Fig. 1a; ESI, Fig. S3†). In addition to the above experimental characterization, 2 was structurally characterized by single-crystal X-ray crystallography. Complex 2 has a six-coordinate distorted octahedral geometry around the CoII-center, possessing O, O−, chelated bi-dentate NO3− anion (Fig. 2; ESI, ES, Fig. S4, Tables T1 and T2†).

OAT reaction of CoII-nitrate complex (2)

So as to understand the NO3− reduction chemistry of 2, we explored its reaction with VCl3 to mimic the OAT based NRs enzymatic reaction. We observed a visible color change from pink to wine-red in the reaction of 2 with VCl3 and a new absorption band (at 370 nm) formed, which is corresponding to the characteristic absorption band of a CoII-nitrosyl ([CoNO]8), 4 (Fig. 3a and 6a†). Astonishingly, 2 upon reaction with VCl3 generated corresponding CoII-nitrosyl complex 4, ([CoNO]8), with V3+Oxo species in both aqueous/or methanol medium at 298 K (Scheme 1; reaction II). It is important to note that 2 did not show any spectral changes in the absence of VCl3, suggesting that 2 is highly stable in H2O/or MeOH and at 298 K (ESI, ES, and Fig. S5†). Finally, the product of NO3− reduction, formed in the reaction of 2 and VCl3, was established to be {CoNO}8 (4) based on various spectroscopic (UV-vis, FT-IR, ESI-MS, NMR) and structural characterization (vide infra). The FT-IR spectrum of 2 showed a peak at 1384 cm−1, characteristic to the CoII bound NO3− stretching frequency which shifted to 1703 cm−1 when 2 was reacted with VCl3, which is characteristic of NO stretching frequency of {CoNO}8 (4). The peak at 1703 cm−1 shifted to 1673 cm−1 when 4 was prepared by reacting 15N-labeled-NO3− (CoII-15NO3−) with VCl3, evidently suggesting the formation of {Co15NO}8 (inset: Fig. 3a; ESI and Fig. S6†). The shifting of NO stretching frequency (Δ = 30 cm−1) indicates that N-atom in NO ligand is derived from CoII-NO3−. The ESI-MS spectrum of 4 showed a prominent peak at m/z 404.2, [(12-TMC) CoII(NO)(BF4)]+ (calc. m/z 404.2), and shifted to 405.2, [[(12-TMC)CoII(15NO)(BF4)]+ (calc m/z 405.2) when the reaction was performed with CoII-15NO3− (Fig. 3b; ESI, Fig. S7†); suggests clearly that NO moiety in 4 is derived from NO3− moiety. The 1H-NMR spectrum of 4 showed the peaks for the protons of 12-TMC ligand frameworks, confirming a low spin diamagnetic CoII center (δH, S = 0) in complex 4 (ESI, Fig. S8†). Further, we have calculated the yield of 4 from NMR spectra using benzene as an internal standard and found to be 90 ± 3% (ESI, Fig. S9†).

![Fig. 1](attachment:fig1.jpg)  
(a) UV-vis spectra of 1 (0.50 mM, brick red line) and 2 (0.50 mM, black line) in CH2CN under Ar at 298 K. Inset: IR spectra of 2−15NO3− (red line) and 2−15NO3− (blue line) in KBr. (b) ESI-MS spectra of 2. The peak at 349.1 is assigned to [(12TMC)CoII(NO3)]+ (calc m/z 349.1). Inset: isotopic distribution pattern for 2−15NO3− (red line) and 2−15NO3− (blue line).

![Fig. 2](attachment:fig2.jpg)  
Displacement ellipsoid plot (20% probability) of 2 at 100 K. Disorder C-atoms of TMC ring, anion and H-atoms have been removed for clarity.

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As a final point, the exact conformation of 4 was provided by its single-crystal X-ray crystallographic analysis (ESI, ES, Fig. S10, Tables T1 and T2†) and comparable with previously reported CoIII–NO/C0–NO/C0 having sp2 hybridized N-atom.20b,21a,27,30,34 The lone pair present on N-atom is responsible for the significant bending of the CoIII–NO/C0 moiety, with Co(1)–N(5)–O(1) bond angles of 128.52 (18)° for 4 and, therefore, further consistent with the assignment of 4 as {CoNO}8 species.

From the final spectrum (black line in Fig. 3a), we have calculated the amount of 4 (90 ± 2%) by comparing its value at 370 nm, since VV-Oxo and VCl3 species does not show any absorption at 370 nm. This value is also in good agreement with the yield calculated from NMR spectroscopy (ESI, Fig. S9†). Further, we had also determined the isolated yield of the formation of 4 and found it to be 90 (±2)%, depicting clearly VCl3 induced NO3− to NO transformation. The reduction of NO3− was observed to be slow; however, it enhanced with an increase in VCl3 amount, suggesting that the NO3− to NO transformation follows the second-order reaction. Upon adding 10 equivalents of VCl3 to the solution of 2 (0.5 mM), the UV-visible band at 370 nm starts forming with a pseudo-first-order rate constant, \( k_{\text{obs}} = 1.2 \times 10^{-1} \text{ s}^{-1} \), and showed the isosbestic points at 418 and 497 nm (Fig. 3a). Upon increasing the concentration of VCl3, the pseudo-first-order rate constants increased proportionally, allowing us to determine a second-order rate constant \( k_2 \) of 2.4 × 10−2 M−1 s−1 (Fig. 4a) for the reaction of 2 with the various equivalents of VCl3 (5, 10, 15, 20, 25).

Confirming VV-Oxo generation in NO3− reduction reaction via OAT

In order to authenticate our proposition of OAT promoted NO3− to NO reduction, we should observe the generation of VV-Oxo species during this transformation. In this regard, we have confirmed the conversion of VCl3 to VV-Oxo species in the NO3− reduction reaction by 51V-NMR. We observed the characteristic peaks of VV-Oxo species in the 51V-NMR spectrum for the reaction mixture obtained after the completion of the reaction of 2 (4 mM) with VCl3 (8 mM) in CD3OD, at 365, 525, and 598 assignable to VOCl3, VOCl(OMe2)2 and VO(OMe2)3, respectively, as reported previously (ESI and Fig. S11†). The observation of VV-Oxo species in the VCl3 promoted NO3− reduction reaction indisputably illustrates that the VCl3 sponsored NO3− to NO conversion should proceed via the two consecutive OAT reactions, where OAT-1 mimics the NRs enzymatic reaction,5b,36 while OAT-2 mimics the phosphorus or sulphur induced OAT transfer reactions (Schemes 1 and 2).26,31

Mechanistic investigation of NO3− reduction

In the biological system, the conversion of NO3− to NO proceeds via a common NO2− intermediate in two consecutive steps (vide
calculated the yield of 1703 cm\(^{-1}\). In this report, it is dreadfully clear that the formation of NO from NO\(_3^-\) could only be accomplished via the VCl\(_3\) induced two consecutive OAT reactions (vide supra), i.e., OAT-1 & OAT-2. Hence, the conversion of NO\(_3^-\) to NO is likely to proceed via a Co\(^{II}\)-NO\(_3^-\) intermediate (3). Although we were unable to isolate the intermediate 3; however, we were able to show its generation by using VCl\(_3\) as a limiting reagent (ES). In the reaction of 2 with 1.0-fold of VCl\(_3\), we observed the generation of 4 with Co\(^{II}\)-NO\(_3^-\) and Co\(^{III}\)-NO\(_3^-\) and confirmed with various spectroscopic measurements. The FT-IR spectrum of the above reaction mixture showed the characteristic peaks for Co\(^{II}\)-NO\(_3^-\) (at 1385 cm\(^{-1}\)), Co\(^{III}\)-NO\(_3^-\) (at 1272 cm\(^{-1}\)) and Co\(^{II}\)-NO\(_3^-\) (at 1703 cm\(^{-1}\)), those shifted to 1358 cm\(^{-1}\), 1245 cm\(^{-1}\) and 1673 cm\(^{-1}\) when \(^{15}\)N-labeled-nitrate complex (3-\(^{15}\)NO\(_3^-\)) reacted with VCl\(_3\), respectively (ESI, Fig. S12a and b†). Also, we have recorded the ESI-MS spectrum of the reaction mixture, which showed the prominent peaks at \(m/z\) 404.2, [[(12-TMC)Co\(^{III}\)-NO\(_3^-(BF_3)\]] (calcd \(m/z\) 404.2), 333.1, [[(12-TMC)Co\(^{II}\)-NO\(_3^-\)]\(^+\)] (calcd \(m/z\) 333.1) and [[(12-TMC)Co\(^{III}\)-NO\(_3^-\)]\(^+\)] (calcd \(m/z\) 349.1), those shifted to 405.2, [[(12-TMC)Co\(^{II}\)-NO\(_3^-\)]\(^+\)] (calcd \(m/z\) 405.2), 334.1, [[(12-TMC)Co\(^{III}\)-NO\(_3^-\)]\(^+\)] (calcd \(m/z\) 344.1) and [[(12-TMC)Co\(^{II}\)-NO\(_3^-\)]\(^+\)] (calcd \(m/z\) 350.1), when the reaction was performed with Co\(^{II}\)-NO\(_3^-\) and VCl\(_3\), respectively (ESI, Fig. S12d and f†). Further, when we reacted 2 with 1.5-fold of VCl\(_3\), we observed the generation of 4 with Co\(^{II}\)-NO\(_3^-\) and confirmed by FT-IR and ESI-MS measurements. The FT-IR spectrum showed the characteristic peaks for Co\(^{II}\)-NO\(_3^-\) (at 1272 cm\(^{-1}\)) and Co\(^{II}\)-NO\(_3^-\) (at 1703 cm\(^{-1}\)), and shifted to 1245 cm\(^{-1}\) (Co\(^{II}\)-\(^{15}\)NO\(_3^-\)) and 1673 cm\(^{-1}\) (Co\(^{III}\)-NO\(_3^-\)) when using \(^{15}\)N-labeled-nitrate complex (3-\(^{15}\)NO\(_3^-\)) (SI, Fig. S13a and b†). The ESI-MS spectrum, for the above reaction mixture, showed the prominent peaks at \(m/z\) 404.2, [[(12-TMC)Co\(^{III}\)-NO\(_3^-(BF_3)\]] (calcd \(m/z\) 404.2), and 333.1, [[(12-TMC)Co\(^{II}\)-NO\(_3^-\)]\(^+\)] (calcd \(m/z\) 333.2), and shifted to 405.2, [[(12-TMC)Co\(^{III}\)-NO\(_3^-\)]\(^+\)] (calcd \(m/z\) 405.2) and 334.1, [[(12-TMC)Co\(^{II}\)-NO\(_3^-\)]\(^+\)] (calcd \(m/z\) 344.1), when using Co\(^{II}\)-\(^{15}\)NO\(_3^-\) as starting reacting material in OAT reaction, correspondingly (ESI, Fig. S13df†). Together, the FT-IR and ESI-MS spectra confirmed that VCl\(_3\) induced reduction of NO\(_3^-\) to NO is going through a Co\(^{II}\)-NO\(_3^-\) (3) intermediate. Furthermore, as described above, when 2 reacted with 2.2-fold of VCl\(_3\), we had observed the generation of only complex 4 with nearly 90 ± 2% yield (vide supra).

With the intention of further validate our concept of Co\(^{II}\)-NO\(_3^-\) species formation in the NO\(_3^-\) reduction reaction, in a control experiment, we explored the VCl\(_3\) induced transformation of Co\(^{II}\)-NO\(_3^-\) to one-electron oxidized Co\(^{II}\)\(^8\) species,\(^{27}\) possibly by the release of one electron which usually gets solvated as observed in other cases,\(^{34}\) and trailed the fate of OAT reaction (Fig. 5). For this reaction, the initial Co\(^{II}\)-NO\(_3^-\) complex was prepared by following the reported literature (Scheme 1, reaction Vla).\(^{26,27}\) Upon addition of one fold VCl\(_3\) to a solution of 3 in MeOH/H\(_2\)O at RT, the color of the reaction solution immediately changed from light pink to wine red, suggesting the generation of Co\(^{II}\)\(^8\) (4),\(^{37}\) and its characteristic absorption band (at 370 nm) appeared in ~1 minute as shown in Fig. 5 and 6b (Scheme 1, reaction Vlb). Also, we have calculated the yield of 4 by comparing its \(ε\) (M\(^{-1}\) cm\(^{-1}\)) value at 370 nm and found it to be (>95 ± 2%). Further, spectral titration data confirmed that the stoichiometric ratio of 3 with VCl\(_3\) was 1 : 1 (ESI, Fig. S14†). Furthermore, the final product (4) was confirmed by the FT-IR and \(^{1}\)H-NMR spectroscopy (ESI, Fig. S15 and S16†).\(^{15,36,28,21,4,27,30}\) Also, the generation of V\(^{3}\)-Oxo species was confirmed by the \(^{51}\)V-NMR (ESI, Fig. S17†). Speedy conversion of 3 to 4 in the presence of VCl\(_3\) justifies our inability to isolate intermediate 3 in the VCl\(_3\) induced conversion of 2 to 4 and supports our supposition of two consecutive OAT reactions in reducing NO\(_3^-\) to NO. We have also determined the second-order rate constant for the reduction of NO\(_2^-\) to NO to understand the reaction mechanism and NO formation fate. The second-order rate constant \((k_2)\) for NO\(_2^-\) reduction was determined by plotting the pseudo-first-order rate constant against various equivalents of VCl\(_3\) (5, 10, 15, 20, and 25) and found to be 34.2 M\(^{-1}\) s\(^{-1}\) (Fig. 4b). Our efforts to isolate the Co\(^{II}\)-NO\(_3^-\)
intermediate in the NO₃⁻ reduction reaction is unsuccessful due to the high reactivity of Co⁵⁺-NO₃⁻ with VCl₃ (OAT-2), which is \( \approx 1420 \) times faster than the second-order rate constant of VCl₃ induced NO₃⁻ to NO reduction \( (k_2 = 2.4 \times 10^{-2} \text{ M}^{-1} \text{s}^{-1}) \).

Spectroscopic and kinetic measurements unambiguously confirmed that the reaction of 3 with VCl₃ generates 4 \([\{\text{CoNO}\}_8]\) plus V⁵⁺Oxo species with a second-order rate constant \( (k_2' = 34.2 \text{ M}^{-1} \text{s}^{-1}) \), suggesting a rapid conversion (Fig. 6b). However, the transformation of 2 to 4 was observed to be a prolonged reaction, based on the spectral measurements (vide infra), in two sequential OAT reactions with a second-order rate constant \( (k_2 = 2.4 \times 10^{-2} \text{ M}^{-1} \text{s}^{-1}) \) via a Co⁵⁺-NO₃⁻ intermediate. This comparison of rate constants \( (k_2 \ll k_2') \) suggests that the formation of NO₃⁻ from NO₂⁻ is a rate-determining step in the NO₃⁻ to NO reduction chemistry. Kinetic measurements (vide supra) confirmed clearly that the first step of the reaction (Scheme 1, pathway II) is the slowest step of the reaction; hence, a rate-determining step. Therefore, the overall second-order rate constant \( (k_2 = 2.4 \times 10^{-2} \text{ M}^{-1} \text{s}^{-1}) \) is equal to the rate constant of the conversion of 2 to 3 (Fig. 4a and 6a). Additionally, the binding constants \( (K_{[\text{Co}(\text{NO})_2]} \text{Co}^{\text{III}} \text{NO}_3^{-}, \text{Co}^{\text{III}} \text{NO}_2^{-}, \text{Co}^{\text{III}} \text{CO} \text{NO}_3^{-}) \) for the generation of different species, Co⁵⁺-NO₃⁻, Co⁵⁺-NO₂⁻ & \{CoNO\}³⁻ in the reaction of \([\text{Co}^{\text{II}}(\text{CH}_3\text{CN})[12\text{TMCl}]^2\] with NO₃⁻, NO₂⁻ & NO, were determined by using Benesi–Hildebrand equation\(^{29}\) and found to be \( 2.3 \times 10^5 \text{ M}^{-1}, 2.5 \times 10^5 \text{ M}^{-1} \) & \( 2.4 \times 10^2 \text{ M}^{-1} \) (ESI, ES, and Fig. S18f), respectively (Scheme 2). Structural parameters and amphiophilic nature of O-atom in coordinated NO₃⁻ & NO₂⁻ species, in their respective complexes,\(^{28}\) and the binding constants calculations further support our proposal of two OAT reactions with different reaction rates \( (r_2 \gg r_1) \). The \( K_{[\text{Co}(\text{NO})_2]} \text{Co}^{\text{III}} \text{NO}_3^{-} \) is higher than that of \( K_{[\text{Co}(\text{NO})_2]} \text{Co}^{\text{III}} \text{NO}_2^{-} \); hence the reaction moves in the forward direction once the NO₃⁻ generates from NO₂⁻ in OAT-1. However, the abstraction of the first non-coordinated O-atom from NO₃⁻ using VCl₃ is somewhat hard due to its less electrophilic nature and more bond strength (bond length[\text{N=O}] = 1.215 Å) compare to other more electrophilic Co⁵⁺-coordinated O-atoms (bond length[\text{N=O}] = 1.267 Å & 1.269 Å); therefore showed a slower rate of OAT-1 \( (r_1) \) than OAT-2 \( (r_2) \) reaction, as proposed theoretically in CO induced Ni-NO₃⁻ reduction chemistry, suggesting the slow rate of NO₃⁻ to NO₂⁻ than NO₂⁻ to NO.\(^{28}\) Kim and co-workers reported that the alteration of O-atom’s electrophilic behavior in NO₃⁻ species, induced by the Sc⁵⁺ metal (Lewis acid) binding, showed the NO₃⁻ to NO₂⁻ reduction, which was not observed in the absence of Sc⁵⁺ ion, suggesting the O-atom activation upon Sc⁵⁺ binding. Discussion on the OAT chemistry\(^{28}\) and metal-induced activation of O-atom\(^{28}\) (vide supra) undoubtedly support our supposition of a faster OAT-2 than the OAT-1, as non-coordinated O-atom of NO₃⁻ is difficult to abstract by VCl₃ than Co⁵⁺-coordinated O-atoms of nitrite moiety.\(^{28}\)

Recent reports on Lewis acid induced OAT reactions showed an increase in the oxidizing power of M-oxygen adducts and their OAT reaction rate,\(^{40}\) which coincides with the activation of N₂ by Lewis acid.\(^{38,41}\) Further, the difference in the rates of the NO₃⁻ & NO₂⁻ reduction were supported by the inert and labile behavior of Co-complexes. High spin Co⁷⁺-complexes, 2 and 3, are labile \( (d^7, S = 3/2) \);\(^{42}\) hence the conversion of 2 to 3 was found to be slow as there is not much change in the CFSE; however, the conversion of labile 3 to an inert 4 \( (d^6, S = 0) \) found to be very fast as there is a huge change in the CFSE, in order to achieve more stable inert electronic configuration.\(^{19,43}\) These results verify our theory of step-wise conversion of NO₃⁻ to NO₂⁻, which further reduces to NO in the presence of VCl₃ in two consecutive OAT reactions.

**Conclusion**

Investigation of insights into the mechanistic aspects of the NO₃⁻ & NO₂⁻ reduction process became a most significant research area in modern-day chemistry as it deals with the biological and environmental aspects.\(^1\) Reduction of NO₃⁻ to NO via NO₂⁻ intermediate species are key steps in biological NO generation (salival NRs followed by NRs in mammalian system)\(^5,44\) and also for the denitriification process (biogeochemical systems).\(^1,45\) Reduction of NO₃⁻ to NO using a single metal complex is still a challenge to the scientific community as two different enzymes play the catalytic role in each step in the biological system.\(^2,3\) In this report, for the very first time, we have shown the direct reduction of NO₃⁻ in a Co⁵⁺-nitrato complex, \([\{12\text{TMCl}\text{Co}^{\text{III}}(\text{NO}_3^-)\}]^+\) (2), to a Co-nitrosyl complex \{CoNO\}³⁻ (4), in the presence of an oxophilic reagent (VCl₃). Mechanistic investigation suggests that the reaction proceeds via a Co⁵⁺-NO₃⁻ (3) species, as observed in the case of biological NRs enzymatic chemistry,\(^5\) in two consecutive OAT reactions. Kinetic measurements suggest that the VCl₃ induced reduction of NO₃⁻ to NO₂⁻ is a rate-determining step \( (k_2 = 2.4 \times 10^{-2}, \text{OAT-1}) \), mimicking the salivary molybdate NRs enzymatic reaction.\(^2\) In the second step \( (\text{OAT-2}) \), a speedy reduction process \( (k_2' = 34.2) \), NO₂⁻ further reduces to NO in the presence of one-fold VCl₃. Isolation of 3 was difficult due to the fast conversion of 3 to 4; however, we could characterize it with various spectroscopic techniques. The results observed in VCl₃ induced NO₃⁻ reduction to NO in two consecutive OAT reactions are found to be in good agreement with our proposed concept. The results are explained in the light of the bond strength and the electrophilic behavior of O-atoms of NO₂⁻/NO₃⁻ ligands and based on the inert & labile nature of Co-complexes. Due to high bond strength and less electrophilic character of metal-unbonded O-atom of NO₃⁻, it showed a slower OAT reaction \( (r_1) \); in contrast, O-atoms of NO₂⁻ moiety is activated due to their binding with Co⁵⁺-center, and the OAT from NO₂⁻ to VCl₃ found to be very fast \( (r_2) \), as observed in Ni-NO₃⁻ reduction chemistry.\(^{28}\) Also, the conversion of high spin 2 to 3 \( (d^6, S = 3/2) \) is slow due to a very less change in the CFSE compare to the transformation of high spin 3 to a low spin 4 \( (d^6, S = 0) \) with much change in the CFSE, additionally support our chemistry. Furthermore, direct generation of 4 from 3 supports our proposition that Co⁵⁺-NO₃⁻ involved as an intermediate species in NO₂⁻ to NO transformation. Tracking the reactions using \(^{15}\text{N}\)-labeled \(^{15}\text{NO}_3^-\) and \(^{15}\text{NO}_2^-\) evidentially suggests that the N-atom in the \{CoNO\}³⁻ species is derived from NO₃⁻ moiety. N-O bond activation\(^{28,31,27,10,34,56}\) of coordinated NO₃⁻ in 2 generates \( 4\)\(^{19}\) hence implying that the OAT reaction of 2 in the presence of VCl₃ generates the Co-nitrosyl species. This work highlights the
first-ever report of VCl₃ encouraged the reduction of NO₃⁻ to NO₂⁻ (NRs activity, OAT-1) followed by another OAT-induced NO₃⁻ to NO transformation (OAT-2). In nature, both the reduction process needs two different enzymes for converting NO₃⁻ to NO₂⁻; hence, the proposed OAT reagent (VCl₃), which is capable of doing the same in a one-shot, has border significance with respect to biological as well as environmental systems.

**Author contributions**

PKK & Kulbir discovered/conceptualized the initial project. Kulbir, SD, MG, PB, & MY carried out the different experiments and gathered the data. PKK, SG & TD helped in interpreting the experimental results. Kulbir and SD write the first draft of the article. PKK & TD have corrected the manuscript, finalized the final draft, and guided during the revision. PKK followed and guided the whole project work.

**Conflicts of interest**

There are no conflicts to declare.

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37 The product of VCl3 induced OAT-2 reaction is {CoNO}8 not {CoNO}6, suggesting a missing electron in the Co–NO2− reduction reaction. One electron loss has been shown in the Scheme 1 and 2 for better understanding, which probably solvated in presence of excess solvent. As a tiny entity, it is very challenging to track an electron in the system. As there is a missing electron in the overall NO2− reduction reaction, we did not describe a more detailed mechanism and based on the product analysis, we proposed the OAT transfer from NO2− moiety.

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