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# 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 ( $\text{NO}_3^-$ ) to nitrite ( $\text{NO}_2^-$ ) in both mammals and plants. In mammals, the salival microbes take part in the generation of the  $\text{NO}_2^-$  from  $\text{NO}_3^-$ , which further produces nitric oxide (NO) either in acid-induced  $\text{NO}_2^-$  reduction or in the presence of nitrite reductases (NiRs). Here, we report a new approach of  $\text{VCl}_3$  ( $\text{V}^{3+}$  ion source) induced step-wise reduction of  $\text{NO}_3^-$  in a  $\text{Co}^{\text{II}}$ -nitrate complex,  $[(12\text{-TMC})\text{Co}^{\text{II}}(\text{NO}_3^-)]^+$  (**2**,  $\{\text{Co}^{\text{II}}-\text{NO}_3^-\}$ ), to a  $\text{Co}^{\text{III}}$ -nitrosyl complex,  $[(12\text{-TMC})\text{Co}^{\text{III}}(\text{NO})]^{2+}$  (**4**,  $\{\text{CoNO}\}^{\text{8}}$ ), bearing an *N*-tetramethylated cyclam (TMC) ligand. The  $\text{VCl}_3$  inspired reduction of  $\text{NO}_3^-$  to NO is believed to occur in two consecutive oxygen atom transfer (OAT) reactions, *i.e.*, **OAT-1** =  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  ( $r_1$ ) and **OAT-2** =  $\text{NO}_2^- \rightarrow \text{NO}$  ( $r_2$ ). In these OAT reactions,  $\text{VCl}_3$  functions as an O-atom abstracting species, and the reaction of **2** with  $\text{VCl}_3$  produces a  $\text{Co}^{\text{III}}$ -nitrosyl ( $\{\text{CoNO}\}^{\text{8}}$ ) with  $\text{V}^{\text{V}}$ -Oxo ( $\{\text{V}^{\text{V}}=\text{O}\}^{\text{3+}}$ ) species, *via* a proposed  $\text{Co}^{\text{II}}$ -nitrito (**3**,  $\{\text{Co}^{\text{II}}-\text{NO}_2^-\}$ ) intermediate species. Further, in a separate experiment, we explored the reaction of isolated complex **3** with  $\text{VCl}_3$ , which showed the generation of **4** with  $\text{V}^{\text{V}}$ -Oxo, validating our proposed reaction sequences of OAT reactions. We ensured and characterized **3** using  $\text{VCl}_3$  as a limiting reagent, as the second-order rate constant of **OAT-2** ( $k_2'$ ) is found to be  $\sim 1420$  times faster than that of the **OAT-1** ( $k_2$ ) reaction. Binding constant ( $K_b$ ) calculations also support our proposition of  $\text{NO}_3^-$  to NO transformation in two successive OAT reactions, as  $K_{b(\text{Co}^{\text{II}}-\text{NO}_2^-)}$  is higher than  $K_{b(\text{Co}^{\text{II}}-\text{NO}_3^-)}$ , hence the reaction moves in the forward direction (**OAT-1**). However,  $K_{b(\text{Co}^{\text{II}}-\text{NO}_2^-)}$  is comparable to  $K_{b(\text{CoNO})^{\text{8}}}$ , and therefore sequenced the second OAT reaction (**OAT-2**). Mechanistic investigations of these reactions using  $^{15}\text{N}$ -labeled- $^{15}\text{NO}_3^-$  and  $^{15}\text{NO}_2^-$  revealed that the N-atom in the  $\{\text{CoNO}\}^{\text{8}}$  is derived from  $\text{NO}_3^-$  ligand. This work highlights the first-ever report of  $\text{VCl}_3$  induced step-wise  $\text{NO}_3^-$  reduction (NRs activity) followed by the OAT induced  $\text{NO}_2^-$  reduction and then the generation of Co-nitrosyl species  $\{\text{CoNO}\}^{\text{8}}$ .

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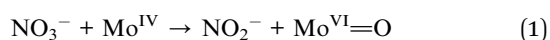
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## Introduction

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 ( $\text{NO}_3^-$ ) to dinitrogen ( $\text{N}_2$ ) conversion  $\{\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow$

$\text{N}_2\}$ , through a series of intermediate gaseous nitrogen oxide products.<sup>1</sup> In mammals and bacteria, inorganic  $\text{NO}_3^-$  and nitrite ( $\text{NO}_2^-$ ) serve as a fundamental storage material of NO for its bio-physiological processes.<sup>2,3</sup> However, in humans, an excessive amount of  $\text{NO}_3^-$  has been discovered to cause gastric cancer and other disorders.<sup>4</sup> To maintain an optimal  $\text{NO}_3^-$  level in the bio-system, commensal bacteria in the human oral cavity play a vital role in converting  $\text{NO}_3^-$  to  $\text{NO}_2^-$  (eqn (1)).<sup>2</sup> In bacteria, molybdenum-based nitrate reductase (NRs) enzymes generate  $\text{NO}_2^-$  *via* an OAT reaction from  $\text{NO}_3^-$  anion.<sup>5</sup> At the bio-physiological level,  $\text{NO}_2^-$  serves as a pool of NO and can easily be transformed to NO, either (i) in non-enzymatic acid-catalyzed  $\text{NO}_2^-$  reduction in the stomach<sup>6,7</sup> or (ii) by Fe and Cu based nitrite reductase (NiRs) enzymes catalyzed reactions (eqn (2)).<sup>8,9</sup>



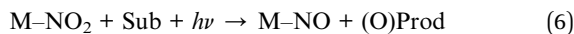
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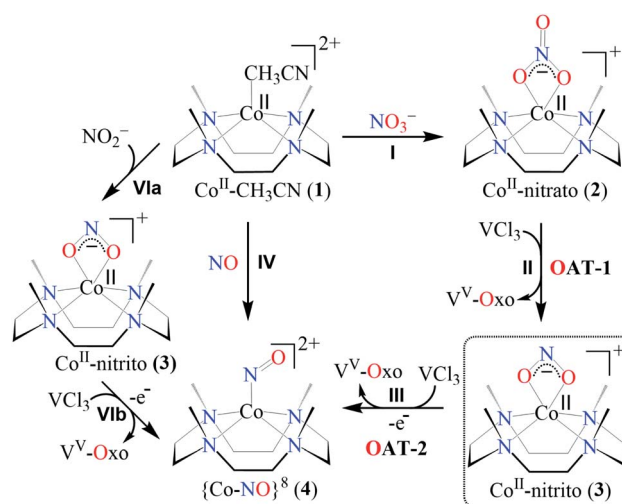
NO is a gaseous secondary messenger in animals, plants, fungi, and bacteria. In plants, NO is involved in different physiological processes, such as plant growth & development, metabolism, aging, defense against pathogens, biotic and abiotic trauma.<sup>10</sup> However, NO regulates various physiological processes in mammals.<sup>11</sup> For instance, NO inadequacy possibly will aggravate the pathogenic effects associated with atherosclerosis, diabetic hypertension, *etc.*<sup>12</sup> Also, the immune response of NO towards the harmful pathogens is related to the oxidized NO species,<sup>13</sup> *i.e.*, peroxy nitrite (PN, ONOO<sup>-</sup>)<sup>13a,14</sup> or nitrogen dioxide (\*NO<sub>2</sub>).<sup>15,16</sup> Hence, balanced production of NO is required to maintain a normal homeostatic bio-physiological condition. In bio-systems, enzymes, *i.e.*, NiRS<sup>8,9,17</sup> and endothelial nitric oxide synthases (eNOSs)<sup>17,18</sup> are available for NO generation. The NOSs enzymes catalyze the biosynthesis of NO from *L*-arginine.<sup>18</sup>

In the case of NO overproduction, nitric oxide dioxygenase (NODs) generates NO<sub>3</sub><sup>-</sup> in the reaction of the iron-dioxygen adduct with NO *via* a proposed PN intermediate,<sup>19</sup> as explored in other biomimetic systems.<sup>19d,20</sup> Also, there are various reports on NO<sub>2</sub><sup>-</sup> formation in nitric oxide monooxygenation (NOM) reaction from metal-nitrosyls in the presence of O<sub>2</sub>, O<sub>2</sub><sup>-</sup> and OH<sup>-</sup>.<sup>19a,20b,21</sup> Oxidized species of NO (NO<sub>3</sub><sup>-</sup> & NO<sub>2</sub><sup>-</sup>) may also generate *via* different oxidative processes (*vide supra*). However, NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> transformation and NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup> to NO conversion (*vis versa*) are critical steps of the denitrification process.<sup>1</sup>

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<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> with metal-Oxo species.<sup>22</sup> Similarly, S. Sarkar and co-workers have reported Mo<sup>IV</sup> mediated reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> to mimic NRs activity.<sup>23</sup> Eunsuk Kim proposed the reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> using the Lewis acid Sc<sup>3+</sup> to activate the OAT reaction from NO<sub>3</sub><sup>-</sup> to Mo metal center.<sup>24</sup> On the other hand, nitrite reduction chemistry is explored widely; Ford and co-workers examined the acid-induced reduction of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub>O in a Fe-porphyrin complex.<sup>25</sup> Warren group described the NiR by using the thiol group.<sup>26</sup> Recently, we have reported acid-induced nitrite reduction to NO.<sup>27</sup> However, the conversion of NO<sub>3</sub><sup>-</sup> to NO using a single catalyst is barely explored; Yunho Lee and co-workers testified Ni catalyzed the transformation of inorganic NO<sub>3</sub><sup>-</sup> to N<sub>2</sub> *via* NO<sub>2</sub><sup>-</sup> intermediate using the carbon monoxide (CO) as oxophilic species.<sup>28</sup>

In biological systems<sup>3,5a</sup> and biomimetic<sup>22,23,27,29</sup> or catalytic reactions,<sup>24</sup> the approach towards converting NO<sub>3</sub><sup>-</sup> to NO is usually a two-enzymes/-catalysts-induced two-step process in two different reactions (*i.e.*, NO<sub>3</sub><sup>-</sup> reduction followed by NO<sub>2</sub><sup>-</sup>

reduction).<sup>5a</sup> However, only a few reports simultaneously carry out both the NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> reduction using a single metal center in a biomimetic system. Here, our eagerness is to mimic the NRs enzymatic reaction followed by the NO<sub>2</sub><sup>-</sup> reduction, sponsored by the same reagent (*i.e.*, single metal-induced two-step NO<sub>3</sub><sup>-</sup> to NO conversion). Herein, we report the NO<sub>3</sub><sup>-</sup> reduction chemistry of a Co<sup>II</sup>-NO<sub>3</sub><sup>-</sup> complex, [(12-TMC)Co<sup>II</sup>(NO<sub>3</sub>)<sup>+</sup>] (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<sub>3</sub> as an oxophilic compound (Scheme 1, reaction II & III). Complex 2 reacts with VCl<sub>3</sub> to form corresponding Co<sup>III</sup>-nitrosyl complex, [(12-TMC)Co<sup>III</sup>(NO)]<sup>2+</sup> (ref. 19d, 20b, 21a, 27 and 30) (4), with V<sup>V</sup>-Oxo ({V<sup>V</sup>=O}<sup>3+</sup>) species, which further decomposes to V<sub>2</sub>O<sub>5</sub>, *via* the formation of a presumed Co<sup>II</sup>-nitrito (3, {Co<sup>II</sup>-NO<sub>2</sub><sup>-</sup>}) intermediate in MeOH or H<sub>2</sub>O at 298 K (Scheme 1, reaction II). Interpretation of various spectral measurements, we have confirmed the generation of 3 with V<sup>V</sup>-Oxo by the transfer of one O-atom from NO<sub>3</sub><sup>-</sup> moiety of 2 to VCl<sub>3</sub> (OAT-1). Further, we observed the generation of 4 with V<sup>V</sup>-Oxo from 3 upon reaction with VCl<sub>3</sub> (OAT-2), under similar reaction conditions, showing the similar OAT induced NO<sub>2</sub><sup>-</sup> reduction reactivity as reported in the case of PPh<sub>3</sub> and sulphur based compounds (thiols and thioethers) (eqn (3)–(6)).<sup>26,31</sup> Combining these two OAT reactions, we can predict the reaction sequences, *i.e.*, the first OAT from NO<sub>3</sub><sup>-</sup> moiety of 2 to VCl<sub>3</sub> and the generation of 3, {OAT-1 = Co<sup>II</sup>-NO<sub>3</sub><sup>-</sup> + VCl<sub>3</sub> → Co<sup>II</sup>-NO<sub>2</sub><sup>-</sup> + VOCl<sub>3</sub> (r<sub>1</sub>)}. Subsequently, the second OAT from NO<sub>2</sub><sup>-</sup> moiety of 3 to another VCl<sub>3</sub> moiety and the generation of 4 {OAT-2 = Co<sup>II</sup>-NO<sub>2</sub><sup>-</sup> + VCl<sub>3</sub> → {CoNO}<sup>8</sup> + VOCl<sub>3</sub> (r<sub>2</sub>)}. Mechanistic investigation using <sup>15</sup>N-labeled-<sup>15</sup>NO<sub>3</sub><sup>-</sup> & <sup>15</sup>NO<sub>2</sub><sup>-</sup> confirmed clearly that the N-atom in the {CoNO}<sup>8</sup> is derived from NO<sub>3</sub><sup>-</sup> anion of 2. To the best of our knowledge, the present work reports the first example of VCl<sub>3</sub> induced conversion of Co<sup>II</sup>-NO<sub>3</sub><sup>-</sup> to {CoNO}<sup>8</sup> in two successive OAT reactions, demonstrating a new mechanistic approach for one-metal induced NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> reduction (NRs activity) followed by NO<sub>2</sub><sup>-</sup> to NO conversion (OAT induced NO<sub>2</sub><sup>-</sup> reduction).



Scheme 1



## Results and discussion

### Preparation of Co<sup>II</sup>-nitrate complex, [(12-TMC)Co<sup>II</sup>(NO<sub>3</sub><sup>-</sup>)]<sup>+</sup> (2)

The primary Co<sup>II</sup>-nitrate complex, [(12-TMC)Co<sup>II</sup>(NO<sub>3</sub><sup>-</sup>)]<sup>+</sup> (2), was prepared by reacting Co<sup>II</sup>-complex, [(12-TMC)Co<sup>II</sup>(NCCH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> (1), with 1 equivalent of NaNO<sub>3</sub> in H<sub>2</sub>O/CH<sub>3</sub>CN (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 ( $\lambda_{\max}$  = 485 nm) changed to a new band ( $\lambda_{\max}$  = 480 nm,  $\epsilon$  = 25 M<sup>-1</sup> cm<sup>-1</sup>) upon addition of 1 equivalent NaNO<sub>3</sub> in CH<sub>3</sub>CN at RT, suggesting the formation of 2 (Fig. 1a). FT-IR spectrum of 2 showed a characteristic peak for Co<sup>II</sup>-bound NO<sub>3</sub><sup>-</sup> anion at 1384 cm<sup>-1</sup> and shifted to 1358 cm<sup>-1</sup> when exchanged with <sup>15</sup>N-labeled-NO<sub>3</sub><sup>-</sup> (<sup>15</sup>N<sup>16</sup>O<sub>3</sub><sup>-</sup>) (Fig. 1a; ESI, Fig. S1†). A wide range <sup>1</sup>H-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 Co<sup>II</sup> metal-center by the Evans' method and found to be 4.46 BM, suggesting a high spin Co<sup>II</sup>-ion in complex 2 (ES, ESI, Fig. 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 <sup>15</sup>N-labeled Na<sup>15</sup>NO<sub>3</sub>, and their mass and isotope distribution pattern corresponds to [(12-TMC)Co<sup>II</sup>(<sup>14</sup>NO<sub>3</sub>)]<sup>+</sup> (calc. *m/z* 349.1) and [(12-TMC)Co<sup>II</sup>(<sup>15</sup>NO<sub>3</sub>)]<sup>+</sup> (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 Co<sup>II</sup>-center, possessing O, O<sup>-</sup>-

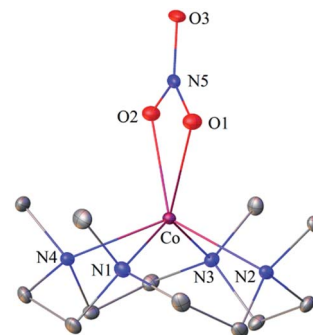


Fig. 2 Displacement ellipsoid plot (20% probability) of 2 at 100 K. Disorder C-atoms of TMC ring, anion and H-atoms have been removed for clarity.

chelated bi-dentate NO<sub>3</sub><sup>-</sup> anion (Fig. 2; ESI, ES, Fig. S4, Tables T1 and T2†).

### OAT reaction of Co<sup>II</sup>-nitrate complex (2)

So as to understand the NO<sub>3</sub><sup>-</sup> reduction chemistry of 2, we explored its reaction with VCl<sub>3</sub> 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 VCl<sub>3</sub> and a new absorption band (at 370 nm) formed, which is corresponding to the characteristic absorption band of a Co<sup>III</sup>-nitrosyl ({CoNO})<sup>8</sup>, 4 (Fig. 3a and 6a).<sup>19d,20b,21a,27,30,32</sup> Astonishingly, 2 upon reaction with VCl<sub>3</sub> generated corresponding Co<sup>III</sup>-nitrosyl complex 4, ({CoNO})<sup>8</sup>,<sup>19d,20b,21a,27,30</sup> with V<sup>V</sup>-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 VCl<sub>3</sub>, suggesting that 2 is highly stable in H<sub>2</sub>O/or MeOH and at 298 K (ESI, ES, and Fig. S5†). Finally, the product of NO<sub>3</sub><sup>-</sup> reduction, formed in the reaction of 2 and VCl<sub>3</sub>, was established to be {CoNO}<sup>8</sup> (4) based on various spectroscopic (UV-vis, FT-IR, ESI-MS, NMR) and structural characterization (*vide infra*).<sup>19d,20b,21a,27,30,32-33</sup> The FT-IR spectrum of 2 showed a peak at 1384 cm<sup>-1</sup>, characteristic to the Co<sup>II</sup> bound NO<sub>3</sub><sup>-</sup> stretching frequency which shifted to 1703 cm<sup>-1</sup> when 2 was reacted with VCl<sub>3</sub>, which is characteristic of NO stretching frequency of {CoNO}<sup>8</sup> (4).<sup>19d,20b,21a,27,30</sup> The peak at 1703 cm<sup>-1</sup> shifted to 1673 cm<sup>-1</sup> when 4 was prepared by reacting <sup>15</sup>N-labeled-NO<sub>3</sub><sup>-</sup> (Co<sup>II</sup>-<sup>15</sup>NO<sub>3</sub><sup>-</sup>) with VCl<sub>3</sub>, evidently suggesting the formation of {Co<sup>15</sup>NO}<sup>8</sup> (inset: Fig. 3a; ESI and Fig. S6†). The shifting of NO stretching frequency ( $\Delta$  = 30 cm<sup>-1</sup>) indicates that N-atom in NO ligand is derived from Co<sup>II</sup>-NO<sub>3</sub><sup>-</sup>. The ESI-MS spectrum of 4 showed a prominent peak at *m/z* 404.2, [(12-TMC)Co<sup>III</sup>(NO)(BF<sub>4</sub>)]<sup>+</sup> (calc. *m/z* 404.2), and shifted to 405.2, [(12-TMC)Co<sup>III</sup>(<sup>15</sup>NO)(BF<sub>4</sub>)]<sup>+</sup> (calc. *m/z* 405.2) when the reaction was performed with Co<sup>II</sup>-<sup>15</sup>NO<sub>3</sub><sup>-</sup> (Fig. 3b; ESI, Fig. S7†); suggests clearly that NO moiety in 4 is derived from NO<sub>3</sub><sup>-</sup> moiety. The <sup>1</sup>H-NMR spectrum of 4 showed the peaks for the protons of 12-TMC ligand frameworks, confirming a low spin diamagnetic Co<sup>III</sup> center (d<sup>6</sup>, *S* = 0) in complex 4 (ESI, Fig. S8†).<sup>32,33</sup> 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†).

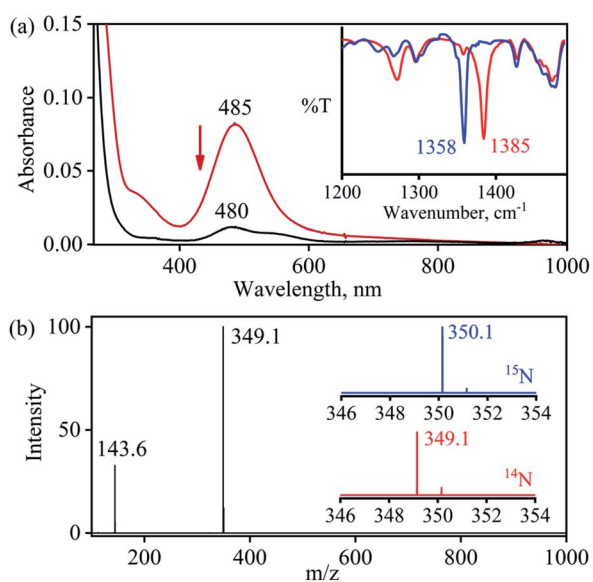


Fig. 1 (a) UV-vis spectra of 1 (0.50 mM, brick red line) and 2 (0.50 mM, black line) in CH<sub>3</sub>CN under Ar at 298 K. Inset: IR spectra of 2-<sup>14</sup>NO<sub>3</sub><sup>-</sup> (red line) and 2-<sup>15</sup>NO<sub>3</sub><sup>-</sup> (blue line) in KBr. (b) ESI-MS spectra of 2. The peak at 349.1 is assigned to [(12-TMC)Co<sup>II</sup>(NO<sub>3</sub>)]<sup>+</sup> (calc. *m/z* 349.1). Inset: isotopic distribution pattern for 2-<sup>14</sup>NO<sub>3</sub><sup>-</sup> (red line) and 2-<sup>15</sup>NO<sub>3</sub><sup>-</sup> (blue line).



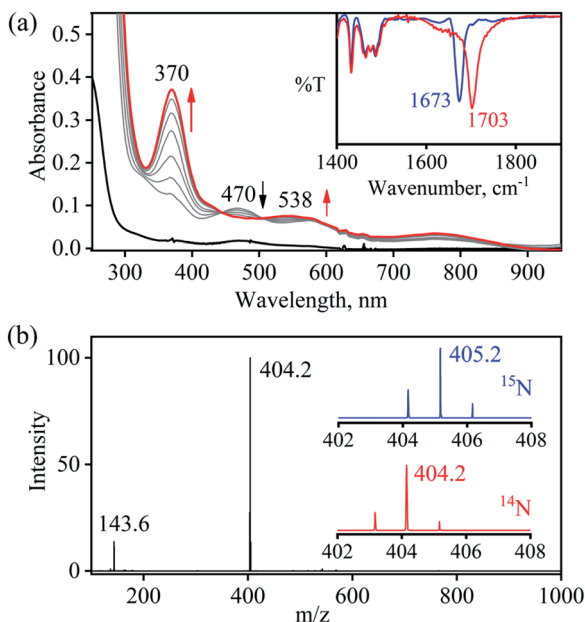


Fig. 3 (a) UV-vis spectral changes of **2** (0.50 mM, black line) upon addition of  $\text{VCl}_3$  (2.2 equiv.) in  $\text{H}_2\text{O}$  at 298 K. Black line (**2**) changed to a red line (**4**) upon addition of  $\text{VCl}_3$ . Inset: IR spectra **4**- $^{14}\text{NO}$  (blue line) and **4**- $^{15}\text{NO}$  (red line) in KBr. (b) ESI-MS spectra of **4**. The peak at 404.2 is assigned to  $[(12\text{TMC})\text{Co}^{\text{III}}(\text{NO})(\text{BF}_4)]^+$  (calcd  $m/z$  404.2). Inset: isotopic distribution pattern for **4**- $^{14}\text{NO}$  (red line) and **4**- $^{15}\text{NO}$  (blue line).

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  $\text{Co}^{\text{III}}\text{-NO}^-/\text{M}\text{-NO}^-$  having  $\text{sp}^2$  hybridized N-atom.<sup>20b,21a,27,30,34</sup> The lone pair present on N-atom is responsible for the significant bending of the  $\text{Co}^{\text{III}}\text{-NO}^-$  moiety, with  $\text{Co}(1)\text{-N}(5)\text{-O}(1)$  bond angles of  $128.52$  ( $18^\circ$ ) for **4** and, therefore, further consistent with the assignment of **4** as  $\{\text{CoNO}\}^8$  species.

From the final spectrum (black line in Fig. 3a), we have calculated the amount of **4** ( $90 \pm 2\%$ ) by comparing its  $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ ) value at 370 nm, since  $\text{V}^{\text{V}}\text{-Oxo}$  and  $\text{VCl}_3$  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  $90$  ( $\pm 2$ )%, depicting clearly  $\text{VCl}_3$  induced  $\text{NO}_3^-$  to  $\text{NO}$  transformation. The reduction of  $\text{NO}_3^-$  was observed to be slow; however, it enhanced with an increase in  $\text{VCl}_3$  amount, suggesting that the  $\text{NO}_3^-$  to  $\text{NO}$  transformation follows the second-order reaction. Upon adding 10 equivalents of  $\text{VCl}_3$  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  $\text{VCl}_3$ , the pseudo-first-order rate constants increased proportionally, allowing us to determine a second-order rate constant ( $k_2$ ) of  $2.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  (Fig. 4a) for the reaction of **2** with the various equivalents of  $\text{VCl}_3$  (5, 10, 15, 20, 25).

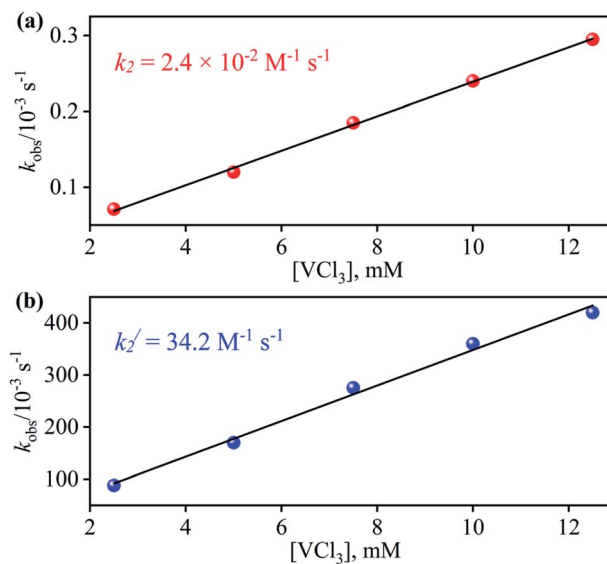


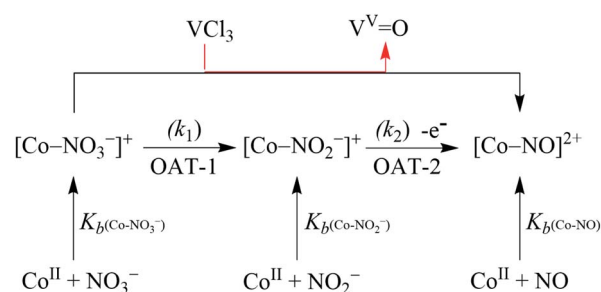
Fig. 4 Plot of  $k_{\text{obs}}$  versus the concentration of  $\text{VCl}_3$  to determine the second order rate constant in the OAT reaction of (a) **2** (b) **3** in  $\text{H}_2\text{O}$  at 298 K.

### Confirming $\text{V}^{\text{V}}\text{-Oxo}$ generation in $\text{NO}_3^-$ reduction reaction via OAT

In order to authenticate our proposition of OAT promoted  $\text{NO}_3^-$  to  $\text{NO}$  reduction, we should observe the generation of  $\text{V}^{\text{V}}\text{-Oxo}$  species during this transformation. In this regard, we have confirmed the conversion of  $\text{VCl}_3$  to  $\text{V}^{\text{V}}\text{-Oxo}$  species in the  $\text{NO}_3^-$  reduction reaction by  $^{51}\text{V}$ -NMR. We observed the characteristic peaks of  $\text{V}^{\text{V}}\text{-Oxo}$  species in the  $^{51}\text{V}$ -NMR spectrum for the reaction mixture obtained after the completion of the reaction of **2** (4 mM) with  $\text{VCl}_3$  (8 mM) in  $\text{CD}_3\text{OD}$ , at  $-365$ ,  $-525$ , and  $-598$  assignable to  $\text{VOCl}_3$ ,  $\text{VOCl}(\text{OMe}_2)_2$  and  $\text{VO}(\text{OMe}_2)_3$ , respectively, as reported previously (ESI and Fig. S11†).<sup>35</sup> The observation of  $\text{V}^{\text{V}}\text{-Oxo}$  species in the  $\text{VCl}_3$  sponsored  $\text{NO}_3^-$  to  $\text{NO}$  conversion should proceed via the two consecutive OAT reactions, where OAT-1 mimics the NRs enzymatic reaction,<sup>5b,36</sup> while OAT-2 mimics the phosphorus or sulphur induced OAT transfer reactions (Schemes 1 and 2).<sup>26,31</sup>

### Mechanistic investigation of $\text{NO}_3^-$ reduction

In the biological system, the conversion of  $\text{NO}_3^-$  to  $\text{NO}$  proceeds via a common  $\text{NO}_2^-$  intermediate in two consecutive steps (*vide*



Scheme 2



*supra*). In this report, it is dreadfully clear that the formation of NO from  $\text{NO}_3^-$  could only be accomplished *via* the  $\text{VCl}_3$  induced two consecutive OAT reactions (*vide supra*), *i.e.*, OAT-1 & OAT-2. Hence, the conversion of  $\text{NO}_3^-$  to NO is likely to proceed *via* a  $\text{Co}^{\text{II}}-\text{NO}_2^-$  intermediate (3). Although we were unable to isolate the intermediate 3; however, we were able to show its generation by using  $\text{VCl}_3$  as a limiting reagent (ES). In the reaction of 2 with 1.0-fold of  $\text{VCl}_3$ , we observed the generation of 4 with  $\text{Co}^{\text{II}}-\text{NO}_3^-$  and  $\text{Co}^{\text{II}}-\text{NO}_2^-$  and confirmed with various spectroscopic measurements. The FT-IR spectrum of the above reaction mixture showed the characteristic peaks for  $\text{Co}^{\text{II}}-\text{NO}_3^-$  (at  $1385\text{ cm}^{-1}$ ),  $\text{Co}^{\text{II}}-\text{NO}_2^-$  (at  $1272\text{ cm}^{-1}$ ) and  $\{\text{Co}^{14}\text{NO}\}^8$  (at  $1703\text{ cm}^{-1}$ ), those shifted to  $1358\text{ cm}^{-1}$ ,  $1245\text{ cm}^{-1}$  and  $1673\text{ cm}^{-1}$  when  $^{15}\text{N}$ -labeled-nitrate complex ( $3\text{-}^{15}\text{NO}_3^-$ ) reacted with  $\text{VCl}_3$ , respectively (ESI, Fig. S12a and b<sup>†</sup>). Also, we have recorded the ESI-MS spectrum of the reaction mixture, which showed the prominent peaks at  $m/z$  404.2,  $[(12\text{-TMC})\text{Co}^{\text{III}}(\text{NO})(\text{BF}_4)]^+$  (calcd  $m/z$  404.2), 333.1,  $[(12\text{-TMC})\text{Co}^{\text{II}}(\text{NO}_2^-)]^+$  (calcd  $m/z$  333.1) and  $[(12\text{-TMC})\text{Co}^{\text{II}}(\text{NO}_3^-)]^+$  (calcd  $m/z$  349.1), those shifted to 405.2,  $[(12\text{-TMC})\text{Co}^{\text{III}}(^{15}\text{NO})(\text{BF}_4)]^+$  (calcd  $m/z$  405.2), 334.1,  $[(12\text{-TMC})\text{Co}^{\text{II}}(^{15}\text{NO}_2^-)]^+$  (calcd  $m/z$  334.1) and  $[(12\text{-TMC})\text{Co}^{\text{II}}(^{15}\text{NO}_3^-)]^+$  (calcd  $m/z$  350.1), when the reaction was performed with  $\text{Co}^{\text{II}}\text{-}^{15}\text{NO}_3^-$  and  $\text{VCl}_3$ , respectively (ESI, Fig. S12c and d<sup>†</sup>). Further, when we reacted 2 with 1.5-fold of  $\text{VCl}_3$ , we observed the generation of 4 with  $\text{Co}^{\text{II}}-\text{NO}_2^-$  and confirmed by FT-IR and ESI-MS measurements. The FT-IR spectrum showed the characteristic peaks for  $\text{Co}^{\text{II}}-\text{NO}_2^-$  (at  $1272\text{ cm}^{-1}$ ) and  $\{\text{Co}^{14}\text{NO}\}^8$  (at  $1703\text{ cm}^{-1}$ ), and shifted to  $1245\text{ cm}^{-1}$  ( $\text{Co}^{\text{II}}\text{-}^{15}\text{NO}_2^-$ ) and  $1673\text{ cm}^{-1}$  ( $\{\text{Co}^{15}\text{NO}\}^8$ ) when using  $^{15}\text{N}$ -labeled-nitrate complex ( $3\text{-}^{15}\text{NO}_3^-$ ) (SI, Fig. S13a and b<sup>†</sup>). The ESI-MS spectrum, for the above reaction mixture, showed the prominent peaks at  $m/z$  404.2,  $[(12\text{-TMC})\text{Co}^{\text{III}}(\text{NO})(\text{BF}_4)]^+$  (calcd  $m/z$  404.2), and 333.1,  $[(12\text{-TMC})\text{Co}^{\text{II}}(\text{NO}_2^-)]^+$  (calcd  $m/z$  333.2), and shifted to 405.2,  $[(12\text{-TMC})\text{Co}^{\text{III}}(^{15}\text{NO})(\text{BF}_4)]^+$  (calcd  $m/z$  405.2) and 333.1,  $[(12\text{-TMC})\text{Co}^{\text{II}}(^{15}\text{NO}_2^-)]^+$  (calcd  $m/z$  334.1), when using  $\text{Co}^{\text{II}}\text{-}^{15}\text{NO}_3^-$  as starting reacting material in OAT reaction, correspondingly (ESI, Fig. S13d<sup>†</sup>). Together, the FT-IR and ESI-MS spectra confirmed that  $\text{VCl}_3$  induced reduction of  $\text{NO}_3^-$  to NO is going through a  $\text{Co}^{\text{II}}-\text{NO}_2^-$  (3) intermediate. Furthermore, as described above, when 2 reacted with 2.2-fold of  $\text{VCl}_3$ , we had observed the generation of only complex 4 with nearly  $90 \pm 2\%$  yield (*vide supra*).

With the intention of further validate our concept of  $\text{Co}^{\text{II}}-\text{NO}_2^-$  species formation in the  $\text{NO}_3^-$  reduction reaction, in a control experiment, we explored the  $\text{VCl}_3$  induced transformation of  $\text{Co}^{\text{II}}-\text{NO}_2^-$  to one-electron oxidized  $\{\text{CoNO}\}^8$  species;<sup>37</sup> possibly by the release of one electron which usually gets solvated as observed in other cases,<sup>38</sup> and trailed the fate of OAT reaction (Fig. 5). For this reaction, the initial  $\text{Co}^{\text{II}}-\text{NO}_2^-$  complex was prepared by following the reported literature (Scheme 1, reaction **Via**).<sup>21a,27</sup> Upon addition of one fold  $\text{VCl}_3$  to a solution of 3 in  $\text{MeOH}/\text{H}_2\text{O}$  at RT, the color of the reaction solution immediately changed from light pink to wine red, suggesting the generation of  $\{\text{CoNO}\}^8$  (4),<sup>37</sup> and its characteristic absorption band (at 370 nm) appeared in  $\sim 1$  minute as shown in Fig. 5 and 6b (Scheme 1, reaction **VIb**). Also, we have calculated the yield of 4 by comparing its  $\epsilon$  ( $\text{M}^{-1}\text{ cm}^{-1}$ ) value at

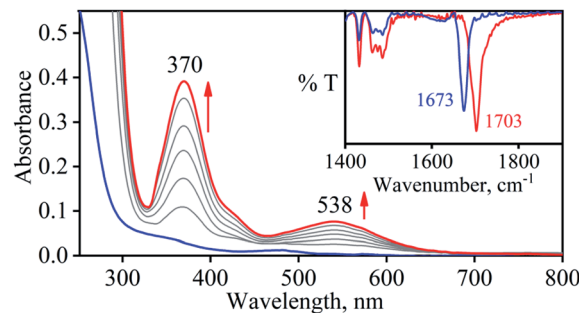


Fig. 5 UV-vis spectral changes of 3 (0.50 mM, blue line) upon addition of  $\text{VCl}_3$  (1 equiv.) in  $\text{H}_2\text{O}$  at 298 K. Blue line (3) changed to red line (4) upon addition of  $\text{VCl}_3$ . Inset: IR spectra 4- $^{14}\text{NO}$  (blue line) and 4- $^{15}\text{NO}$  (red line) in KBr.

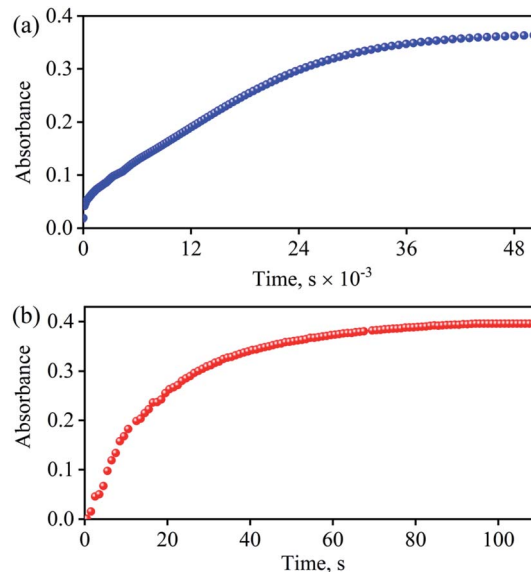


Fig. 6 (a) Time course of the formation of 4 (blue circles) monitored at 370 nm upon addition  $\text{VCl}_3$  (2.2 equiv.) to a solution of 2 (0.5 mM) in  $\text{H}_2\text{O}$  at 298 K. (b) Time course of the formation of 4 (Red circles) monitored at 370 nm upon addition  $\text{VCl}_3$  (1 equiv.) to a solution of 3 (0.5 mM) in  $\text{H}_2\text{O}$  at 298 K.

370 nm and found it to be ( $>95 \pm 2\%$ ). Further, spectral titration data confirmed that the stoichiometric ratio of 3 with  $\text{VCl}_3$  was 1 : 1 (ESI, Fig. S14<sup>†</sup>). Furthermore, the final product (4) was confirmed by the FT-IR and  $^1\text{H-NMR}$  spectroscopy (ESI, Fig. S15 and S16<sup>†</sup>).<sup>19d,20b,21a,27,30</sup> Also, the generation of  $\text{V}^{\text{V}}$ -Oxo species was confirmed by the  $^{51}\text{V-NMR}$  (ESI, Fig. S17<sup>†</sup>). Speedy conversion of 3 to 4 in the presence of  $\text{VCl}_3$  justifies our inability to isolate intermediate 3 in the  $\text{VCl}_3$  induced conversion of 2 to 4 and supports our supposition of two consecutive OAT reactions in reducing  $\text{NO}_3^-$  to NO. We have also determined the second-order rate constant for the reduction of  $\text{NO}_2^-$  to NO to understand the reaction mechanism and NO formation fate. The second-order rate constant ( $k_2'$ ) for  $\text{NO}_2^-$  reduction was determined by plotting the pseudo-first-order rate constant against various equivalents of  $\text{VCl}_3$  (5, 10, 15, 20, and 25) and found to be  $34.2\text{ M}^{-1}\text{ s}^{-1}$  (Fig. 4b). Our efforts to isolate the  $\text{Co}^{\text{II}}-\text{NO}_2^-$



intermediate in the  $\text{NO}_3^-$  reduction reaction is unsuccessful due to the high reactivity of  $\text{Co}^{\text{II}}\text{-NO}_2^-$  with  $\text{VCl}_3$  (**OAT-2**), which is  $\sim 1420$  times faster than the second-order rate constant of  $\text{VCl}_3$  induced  $\text{NO}_3^-$  to  $\text{NO}$  reduction ( $k_2 = 2.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ).

Spectroscopic and kinetic measurements undeniably confirmed that the reaction of **3** with  $\text{VCl}_3$  generates **4** ( $\{\text{CoNO}\}^8$ ) plus  $\text{V}^{\text{V}}$ -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  $\text{Co}^{\text{II}}\text{-NO}_2^-$  intermediate. This comparison of rate constants ( $k_2 \lll k_2'$ ) suggests that the formation of  $\text{NO}_2^-$  from  $\text{NO}_3^-$  is a rate-determining step in the  $\text{NO}_3^-$  to  $\text{NO}$  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 ( $K_{\text{b}(\text{Co}^{\text{II}}\text{-NO}_3^-)}$ ,  $K_{\text{b}(\text{Co}^{\text{II}}\text{-NO}_2^-)}$ , &  $K_{\text{b}(\{\text{CoNO}\}^8)}$ ) for the generation of different species,  $\text{Co}^{\text{II}}\text{-NO}_3^-$ ,  $\text{Co}^{\text{II}}\text{-NO}_2^-$  &  $\{\text{CoNO}\}^8$  in the reaction of  $[\text{Co}^{\text{II}}(\text{CH}_3\text{CN})(12\text{TMC})]^{2+}$  with  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  &  $\text{NO}$ , were determined by using Benesi–Hildebrand equation<sup>39</sup> and found to be  $2.3 \times 10^2 \text{ M}^{-1}$ ,  $2.5 \times 10^3 \text{ M}^{-1}$  &  $2.4 \times 10^3 \text{ M}^{-1}$  (ESI, ES, and Fig. S18<sup>†</sup>), respectively (Scheme 2). Structural parameters and ambiphilic nature of O-atom in coordinated  $\text{NO}_3^-$  &  $\text{NO}_2^-$  species, in their respective complexes,<sup>28</sup> and the binding constants calculations further support our proposal of two OAT reactions with different reaction rates ( $r_2 \gg r_1$ ). The  $K_{\text{b}(\text{Co}^{\text{II}}\text{-NO}_2^-)}$  is higher than that of  $K_{\text{b}(\text{Co}^{\text{II}}\text{-NO}_3^-)}$ ; hence the reaction moves in the forward direction once the  $\text{NO}_2^-$  generates from  $\text{NO}_3^-$  in **OAT-1**. However, the abstraction of the first non-coordinated O-atom from  $\text{NO}_3^-$  using  $\text{VCl}_3$  is somewhat hard due to its less electrophilic nature and more bond strength (bond length $_{\text{(N-O)}} = 1.215 \text{ \AA}$ ) compare to other more electrophilic  $\text{Co}^{2+}$ -coordinated O-atoms (bond length $_{\text{(N-O)}} = 1.267 \text{ \AA}$  &  $1.269 \text{ \AA}$ ); therefore showed a slower rate of **OAT-1** ( $r_1$ ) than **OAT-2** ( $r_2$ ) reaction, as proposed theoretically in CO induced Ni- $\text{NO}_3^-$  reduction chemistry, suggesting the slow rate of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  than  $\text{NO}_2^-$  to  $\text{NO}$ .<sup>28</sup> Kim and co-workers reported that the alteration of O-atom's electrophilic behavior in  $\text{NO}_3^-$  species, induced by the  $\text{Sc}^{3+}$  metal (Lewis acid) binding, showed the  $\text{NO}_3^-$  to  $\text{NO}_2^-$  reduction, which was not observed in the absence of  $\text{Sc}^{3+}$  ion, suggesting the O-atom activation upon  $\text{Sc}^{3+}$  binding. Discussion on the OAT chemistry<sup>28</sup> and metal-induced activation of O-atom<sup>24</sup> (*vide supra*) undoubtedly support our supposition of a faster **OAT-2** than the **OAT-1**, as non-co-ordinated O-atom of  $\text{NO}_3^-$  is difficult to abstract by  $\text{VCl}_3$  than  $\text{Co}^{2+}$ -co-ordinated O-atoms of nitrite moiety.<sup>24,28</sup> Recent reports on Lewis acid induced OAT reactions showed an increase in the oxidizing power of M-oxygen adducts and their OAT reaction rate,<sup>40</sup> which coincides with the activation of  $\text{N}_2$  by Lewis acid.<sup>28,41</sup> Further, the difference in the rates of the  $\text{NO}_3^-$  &  $\text{NO}_2^-$  reduction were supported by the inert and labile behavior of Co-complexes. High spin  $\text{Co}^{\text{II}}$ -complexes, **2** and **3**, are labile ( $d^7$ ,  $S = 3/2$ );<sup>42</sup> 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.<sup>19d,43</sup> These results verify our theory of step-wise conversion of  $\text{NO}_3^-$  to  $\text{NO}_2^-$ , which further reduces to  $\text{NO}$  in the presence of  $\text{VCl}_3$  in two consecutive OAT reactions.

## Conclusion

Investigation of insights into the mechanistic aspects of the  $\text{NO}_3^-$  &  $\text{NO}_2^-$  reduction process became a most significant research area in modern-day chemistry as it deals with the biological and environmental aspects.<sup>1</sup> Reduction of  $\text{NO}_3^-$  to  $\text{NO}$  *via*  $\text{NO}_2^-$  intermediate species are key steps in biological NO generation (salivary NRs followed by NiRs in mammalian system)<sup>5,44</sup> and also for the denitrification process (biogeochemical systems).<sup>1,45</sup> Reduction of  $\text{NO}_3^-$  to  $\text{NO}$  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.<sup>2,3</sup> In this report, for the very first time, we have shown the direct reduction of  $\text{NO}_3^-$  in a  $\text{Co}^{\text{II}}$ -nitrate complex,  $[(12\text{TMC})\text{Co}^{\text{II}}(\text{NO}_3^-)]^+$  (**2**), to a Co-nitrosyl complex  $\{\text{CoNO}\}^8$  (**4**), in the presence of an oxophilic reagent ( $\text{VCl}_3$ ). Mechanistic investigation suggests that the reaction proceeds *via* a  $\text{Co}^{\text{II}}\text{-NO}_2^-$  (**3**) species, as observed in the case of biological NRs enzymatic chemistry,<sup>5</sup> in two consecutive OAT reactions. Kinetic measurements suggest that the  $\text{VCl}_3$  induced reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  is a rate-determining step ( $k_2 = 2.4 \times 10^{-2}$ , **OAT-1**), mimicking the salivary molybdate NRs enzymatic reaction.<sup>5</sup> In the second step (**OAT-2**), a speedy reduction process ( $k_2' = 34.2$ ),  $\text{NO}_2^-$  further reduces to  $\text{NO}$  in the presence of one-fold  $\text{VCl}_3$ . 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  $\text{VCl}_3$  induced  $\text{NO}_3^-$  reduction to  $\text{NO}$  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  $\text{NO}_3^-/\text{NO}_2^-$  ligands and based on the inert & labile nature of Co-complexes. Due to high bond strength and less electrophilic character of metal-unbound O-atom of  $\text{NO}_3^-$ , it showed a slower OAT reaction ( $r_1$ ); in contrast, O-atoms of  $\text{NO}_2^-$  moiety is activated due to their binding with  $\text{Co}^{\text{II}}$ -center, and the OAT from  $\text{NO}_2^-$  to  $\text{VCl}_3$  found to be very fast ( $r_2$ ), as observed in Ni- $\text{NO}_3^-$  reduction chemistry.<sup>28</sup> Also, the conversion of high spin **2** to **3** ( $d^7$ ,  $S = 3/2$ ) 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  $\text{Co}^{\text{II}}\text{-NO}_2^-$  involved as an intermediate species in  $\text{NO}_3^-$  to  $\text{NO}$  transformation. Tracking the reactions using  $^{15}\text{N}$ -labeled- $^{15}\text{NO}_3^-$  and  $^{15}\text{NO}_2^-$  evidently suggests that the N-atom in the  $\{\text{CoNO}\}^8$  species is derived from  $\text{NO}_3^-$  moiety. N-O bond activation<sup>20b,21a,27,30,34a,34c</sup> of coordinated  $\text{NO}_3^-$  in **2** generates **4**,<sup>19d</sup> hence implying that the OAT reaction of **2** in the presence of  $\text{VCl}_3$  generates the Co-nitrosyl species. This work highlights the



first-ever report of  $\text{VCl}_3$  encouraged the reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  (NRs activity, OAT-1) followed by another OAT induced  $\text{NO}_2^-$  to NO transformation (OAT-2). In nature, both the reduction process needs two different enzymes for converting  $\text{NO}_3^-$  to NO; hence, the proposed OAT reagent ( $\text{VCl}_3$ ), 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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