

Cite this: *Dalton Trans.*, 2023, **52**, 16492Mechanistic insights into nitric oxide oxygenation (NOO) reactions of {CrNO}⁵ and {CoNO}⁸†Akshaya Keerthi C. S.,^a Sandip Das,^b Kulbir,^a Prabhakar Bhardwaj,^a Md Palashuddin Sk^b and Pankaj Kumar^{*a}

Here, we report the nitric oxide oxygenation (NOO) reactions of two distinct metal nitrosyls {Co–nitrosyl ($S = 0$) vs. Cr–nitrosyl ($S = 1/2$)}. In this regard, we synthesized and characterized [(BPMEN)Co(NO)]²⁺ ({CoNO}⁸, **1**) to compare its NOO reaction with that of [(BPMEN)Cr(NO)(Cl)]⁺ ({CrNO}⁵, **2**), having a similar ligand framework. Kinetic measurements showed that {CrNO}⁵ is thermally more stable than {CoNO}⁸. Complexes **1** and **2**, upon reaction with the superoxide anion (O₂^{•−}), generate [(BPMEN)Co^{II}(NO₂[−])₂] (Co^{II}–NO₂[−], **3**) and [(BPMEN)Cr^{III}(NO₂[−])(Cl)]⁺ (Cr^{III}–NO₂[−], **4**), respectively, with O₂ evolution. Furthermore, analysis of these NOO reactions and tracking of the N-atom using ¹⁵N-labeled NO (¹⁵NO) revealed that the N-atoms of **3** (Co^{II}–¹⁵NO₂[−]) and **4** (Cr^{III}–¹⁵NO₂[−]) derive from the nitrosyl (¹⁵NO) moieties of **1** and **2**, respectively. This work represents a comparative study of oxidation reactions of {CoNO}⁸ vs. {CrNO}⁵, showing different rates of the NOO reactions due to different thermal stability. To complete the NOM cycle, we reacted **3** and **4** with NO, and surprisingly, only **3** generated {CoNO}⁸ species, while **4** was unreactive towards NO. Furthermore, the phenol ring nitration test, performed using 2,4-di-*tert*-butylphenol (2,4-DTBP), suggested the presence of a proposed peroxyxynitrite (PN) intermediate in the NOO reactions of **1** and **2**.

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Introduction

Nitric oxide (NO) is a simple gas earlier thought to be an atmospheric pollutant and poison.¹ In recent years, NO has been proven to be one of the essential signaling gases participating in a wide range of physiological processes, *i.e.*, neurotransmission, vascular regulation, disaggregation of platelets, immune response towards multiple infections, *etc.*^{1,2} Inadequate NO generation causes biological dysfunctions (*vide supra*) and causes various diseases, such as diabetic hypertension,³ kidney disease,³ atherosclerosis,⁴ cognitive dysfunctions,⁵ *etc.*⁶ Hence, to maintain biological homeostasis, two families of biological enzymes, *i.e.*, nitric oxide synthases (NOSs)^{7,8} and nitrite reductases (NiRs),⁹ are involved in NO biosynthesis. When overproduced, NO leads to cytotoxicity by forming reactive nitrogen species (RNS), *i.e.*, peroxyxynitrite (PN, OONO[−])¹⁰ and nitrogen dioxide

(NO₂),¹¹ upon reaction with dioxygen (O₂),¹² the superoxide anion (O₂^{•−}),¹³ or hydrogen peroxide (H₂O₂).¹⁴ Thus, maintaining the optimal level of NO in the biosystem is necessary. Therefore, microbial/or mammalian systems oxidize excess NO to biologically benign nitrate (NO₃[−]) using Fe-containing nitric oxide dioxygenase (NOD)¹⁵ enzymes *via* a plausible PN intermediate.¹⁶ In some bacteria and archaea, a unique di-iron protein carries out the process of NO detoxification by reducing it into N₂O.¹⁷

Bio-mimetic modeling of NOD enzymes and their mechanistic investigation proposed the formation of a metal–dioxygen adduct upon reaction with O₂, which then reacts with NO to generate NO₃[−] *via* a proposed M–PN intermediate.^{15b,18} Several models of metal–dioxygen (M–O₂) intermediates were developed to understand/establish the actual mechanism of the NOD reaction.¹⁹ In this regard, Kurtikyan *et al.* studied oxycoboglobin's NOD reaction that generates Co–NO₃[−] at low temperatures.²⁰ Also, Cr^{IV}–O₂^{2−} and Co^{III}–O₂^{2−} species produced Cr^{III}–NO₃[−] and Co^{II}–NO₃[−] species when reacted with NO, respectively.^{19c,21} In addition to NOD reaction products, NO-mono-oxygenation (NOM) products were also observed in several metal–dioxygen adduct reactions with NO. Karlin and coworkers observed Cu^{II}–NO₂[−] in the reaction of Cu^{II}–O₂^{•−} with NO *via* a PN intermediate.²² Nam and coworkers observed a NOM product formation (Cr^{III}–NO₂[−]) in the reaction of Cr^{III}–O₂^{•−} with NO *via* a Cr^{IV}=O species.^{19b} Contrarily, the reaction

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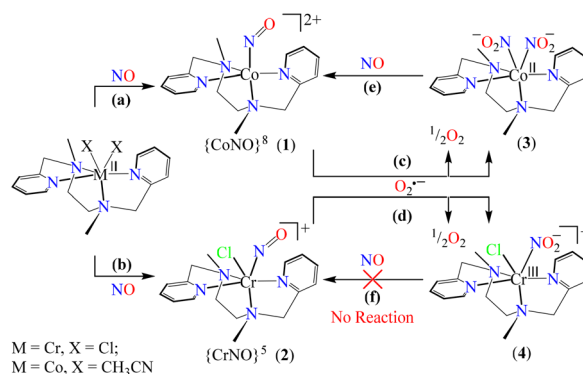


of Fe-O₂²⁻ with NO⁺ led to an Fe^{III}-NO₃⁻ complex, a NOD reaction product.^{19a} In another case, Fe-O₂²⁻ and Mn-O₂²⁻ bearing the TAML ligand led to the formation of Fe^{III}-NO₃⁻ and Mn^{IV}=O + NO₂ *via* a presumed PN intermediate, respectively.²³ Thus, the metal center considerably controls the NO oxygenation reaction (NOD *vs.* NOM). In this regard, several comparative studies were performed to understand the role of the metal center. Recently, we have studied the comparative NO oxygenation reactivity of Co-O₂²⁻ and Ni-O₂²⁻ bearing a similar 12TMC ligand framework that generates Co^{II}-NO₂⁻ and Ni^{II}-NO₃⁻ as the end products.²⁴ Groves and coworkers reported the formation of Fe^{IV}=O and NO₂ in the reaction of methHb with the PN molecule.²⁵ Considerable work is underway and has also already been performed to establish the presence of a PN intermediate in NO oxidation reactions, *i.e.*, IR,^{19f,20,26} EPR,^{19f} *etc.*; however, the same is under debate. In contrast, Pacheco and the group proposed that the NOD reaction with oxymyoglobin does not share the PN intermediate.²⁷ Further supported by Moëne-Loccoz and coworkers' work on the NOD reaction of oxymyoglobin, it is portentous that the millisecond intermediate is an Fe^{III}-NO₃⁻ species and not a PN intermediate.²⁸ Although the PN intermediate was not detected in the oxy-globin protein's NOD reaction, the experimental results proposed a short-lifetime intermediate before forming metal-NO₃⁻.^{19e} In biology, an additional pathway of the NOD reaction has also been presented, which suggests Fe-NO formation upon reaction of NO with the Fe-center of Hb, and then it reacts with O₂, resulting in NO₃⁻ formation.²⁹ However, a reverse pathway was investigated in detail by Stuehr and coworkers by taking a series of different Fe-NO species.³⁰

Hence, the NO activation using metal ions has been an active field of research for chemists and biochemists for many years to understand its coordination chemistry and reactivity.³¹ In various biological enzymatic reactions, *i.e.*, nitrogen fixation,³² NiR reaction,^{24,33} NOD reactions,^{15a,34} *etc.*, M-NOs are the key intermediates. In recent years, very few M-NOs have been prepared and explored for their various reactions to understand and mimic the biological M-NOs' reactivity.^{15c,31-d,35} Among them, only a few M-NOs were examined for NO-oxidation reactions, *i.e.*, reactions with dioxygen,¹² superoxides,¹³ base,³⁶ and H₂O.³⁷ Oxidation of M-NOs generates NO mono- or di-oxygenated products, usually depending on the type of M-NO and stability of the intermediate involved. {CoNO}⁸ produced NO₂⁻ when reacted with O₂;³⁸ in another example, {FeNO}⁷ formed NO₂⁻ from NO oxidation.³⁹ Recently, Nam and coworkers showed the oxidation of {CoNO}⁸ to Co^{II}-NO₃⁻ and Co^{II}-NO₂⁻ + O₂ upon reaction with O₂ and O₂^{•-}, respectively.^{35b} Also, Mondal and coworkers reported the NO₃⁻ generation from {CoNO}⁸ and {CuNO}¹⁰ species upon reaction with hydrogen peroxide (H₂O₂) *via* a proposed PN intermediate.⁴⁰ In contrast to {CoNO}⁸ reactivity towards O₂^{•-}, {MnNO}⁶ upon reaction with O₂^{•-} generated Mn^{III}-NO₃⁻ *via* a presumed PN intermediate.⁴¹ As the oxidized products of M-NOs depend upon the choice of the metal center, their oxidation state, and the intermediate involved in the reaction, a deep study is

required to establish the actual mechanism of the M-NO oxidation reactions.

Among various metal-nitrosyl complexes, {CrNO}⁵ and {CoNO}⁸ species are widely explored and known to be reasonably stable with linear and bent metal-NO coordination, respectively.^{24,33e,35b,42} Thus, to understand the NO oxidation reactions of metal-nitrosyl complexes, we prepared {CrNO}⁵ (*S* = 1/2) and {CoNO}⁸ (*S* = 0), having different spin states/magnetic properties with similar ligand frameworks. Therefore, [(BPMEN)Co(NO)]²⁺ ({CoNO}⁸, **1**) and [(BPMEN)Cr(NO)(Cl)]⁺ ({CrNO}⁵, **2**) complexes⁴³ (BPMEN = *N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane) were explored for their reactivity towards O₂^{•-} (KO₂/18-crown-6), to understand the effect of the metal center and the spin state/magnetic properties (Scheme 1). Following our previous reports,^{43,44} we synthesized new {CoNO}⁸ and {CrNO}⁵ complexes and calculated various physical parameters for **1** and **2** to determine their thermal stability, the NO oxidation reactions and the intermediates involved (Scheme 1, reactions a and b). Complex **1** generates a Co^{II}-nitrito complex [(BPMEN)Co^{II}(NO₂⁻)₂] (Co^{II}-NO₂⁻, **3**) + O₂ in the presence of O₂^{•-} *via* a proposed thermally unstable [Co-PN]⁺ species (Scheme 1, reaction c). However, **2** generates an oxidized Cr^{III}-nitrito complex [(BPMEN)Cr^{III}(NO₂⁻)Cl]⁺ (Cr^{III}-NO₂⁻, **4**) + O₂ upon reaction with O₂^{•-} *via* a proposed [Cr-PN]⁺ intermediate species (Scheme 1, reaction d). The phenol ring nitration test performed using 2,4-DTBP suggested the presence of the proposed PN intermediate in the NOM reactions of **1** and **2**. Mechanistic studies using ¹⁵N-labeled nitric oxide (¹⁵NO) revealed that the N-atoms of **3** (Co^{II}-¹⁵NO₂⁻) and **4** (Cr^{III}-¹⁵NO₂⁻) were derived from the ¹⁵NO moieties of **1** and **2**, respectively. In addition, to complete the NOM cycle, we reacted **3** and **4** with NO, which showed the formation of {CoNO}⁸ from **3**, while **4** was unreactive to NO (Scheme 1, reactions e and f). The equilibrium constant (*K*_{eq}) of the formation of **2** is ~25 times that of **1**, suggesting that **2** is more stable than **1**; hence, it also explains why the reaction of **2** with O₂^{•-} is slower than that of **1**. In both reactions, we observed NO₂⁻ (NOM) formation; however, only complex **3** could generate the initial M-NO (**1**) while **4** was unreactive towards NO.



Scheme 1 NO activation at Cr and Co centers and NOO reactions of **1** and **2**.



Results and discussion

Synthesis of Co-nitrosyl, [(BPMEN)Co(NO)]²⁺ ({CoNO}⁸, **1**)

The initial Co^{II}-complex [(BPMEN)Co^{II}(CH₃CN)₂]²⁺ (Co-1) was synthesized by adding the BPMEN ligand to a stirring solution of [Co^{II}(H₂O)₆](BF₄)₂ and characterized with various spectroscopic measurements (Fig. 2, see the ESI and Experimental section (ES), Fig. S1†). The addition of excess NO to the CH₃CN solution of Co-1 at 233 K under an Ar atmosphere resulted in the generation of [(BPMEN)Co(NO)]²⁺ ({CoNO}⁸, **1**) (λ_{\max} = 375, ϵ = 956 M⁻¹ cm⁻¹, red line) within one hour (Fig. 1a and ESI Fig. S2a†) (Scheme 1, reaction a). The FT-IR spectrum also reveals that the NO moiety is bound to a Co-center, suggesting a bent NO with a typical Co–NO stretching at 1653 cm⁻¹ (inset: Fig. 1a; ESI, Fig. S2b†).^{33e,35a,b} Electrospray ionization mass spectrometry (ESI-MS) of **1** showed a promi-

nent ion peak at m/z 376.1, whose mass and isotope distribution patterns correspond to [(BPMEN)Co(NO)(OH⁻)]⁺ (calcd m/z 376.1) (ESI,† Fig. 1b). Upon substitution of the NO moiety with ¹⁵N-labeled ¹⁵NO in **1**,^{24,45} the mass peak corresponding to [Co(BPMEN)(¹⁵NO)(OH⁻)]⁺ appears at m/z 377.1 (calcd m/z 377.1) (inset: Fig. 1b; ESI, Fig. S2c†), suggesting that the NO moiety is bound to the Co-center. The Evans' method established a high-spin Co^{II}-center ($S = 3/2$) in Co-1 (ESI, Fig. S1e†);⁴⁶ hence, its ¹H NMR does not show any signal for aromatic/aliphatic protons in the normal range (ESI, Fig. S3a†). However, we observed these signals in complex **1**, confirming a diamagnetic Co-center (ESI, Fig. S3b†). The redox potential of **1** was determined using a cyclic voltammogram (ESI, Fig. S3c†). To perform NOO experiments, we prepared/isolated **1** by purging Co-1 with excess NO gas in CH₃CN at 233 K under Ar (ESI, ES;† yield: 76%).

NO oxygenation reaction of the {CoNO}⁸ complex (**1**)

To explore the NO oxygenation (NOO) reaction of {CoNO}⁸, we reacted the new Co–NO complex [(BPMEN)Co(NO)]²⁺ ({CoNO}⁸, **1**; $S = 0$) with O₂^{•-}. The addition of O₂^{•-} to a solution of **1** resulted in the generation of [(BPMEN)Co^{II}(NO₂⁻)₂] (Co^{II}-NO₂⁻, **3**). The characteristic UV-vis absorption bands of **1** (λ_{\max} = 375 nm, ϵ = 956 M⁻¹ cm⁻¹) changed to a new band (λ_{\max} = 360 nm, ϵ = 4040 M⁻¹ cm⁻¹), which corresponds to **3**, within 5 minutes in CH₃CN at 298 K under Ar (Fig. 3a; ESI, Fig. S5†). However, **1** does not show any spectral changes in the absence of O₂^{•-}, ruling out the natural decomposition of **1** generating free NO followed by the reaction with O₂^{•-} (ESI, Fig. S5b†). Complex **3** was determined to be [(BPMEN)Co^{II}(NO₂⁻)₂] based on various spectroscopic and single-crystal X-ray structural

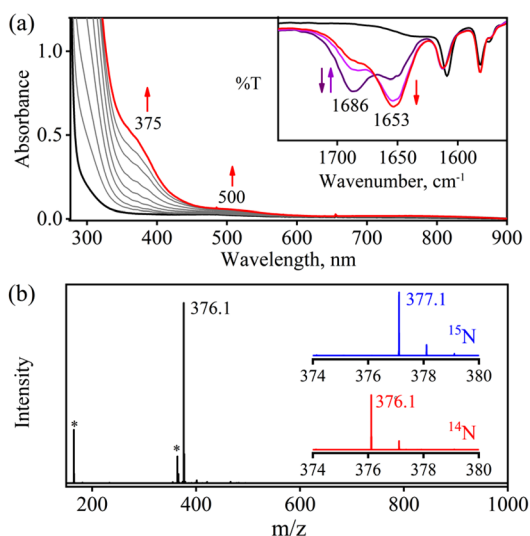


Fig. 1 (a) UV-vis spectral change of Co-1 (0.5 mM, black line) upon addition of NO(g) in CH₃CN under Ar at 233 K. Inset: Solution IR spectra of the formation of **1** (red line). (b) ESI-MS spectra of **1**. The peak at 376.1 is assigned to [(BPMEN)Co^{II}(NO)(OH⁻)]⁺ (calcd m/z 376.1). Inset: Isotopic distribution patterns of **1**-¹⁴NO (red line) and **1**-¹⁵NO (blue line). The peaks at m/z 364.1 and 364.5 marked with asterisks are assigned to [(BPMEN)Co(Cl⁻)]⁺ and [(BPMEN)Co]²⁺, respectively.

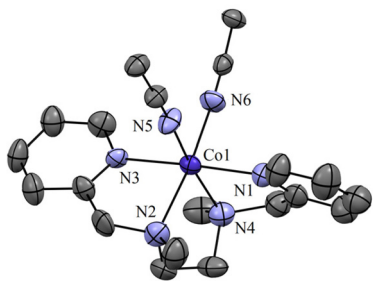


Fig. 2 Displacement ellipsoid plot (30% probability) of Co-1 at 298 K. Anions and H-atoms have been removed for clarity.

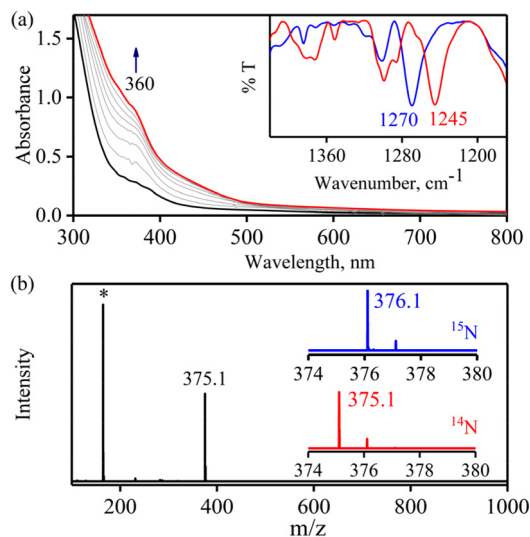
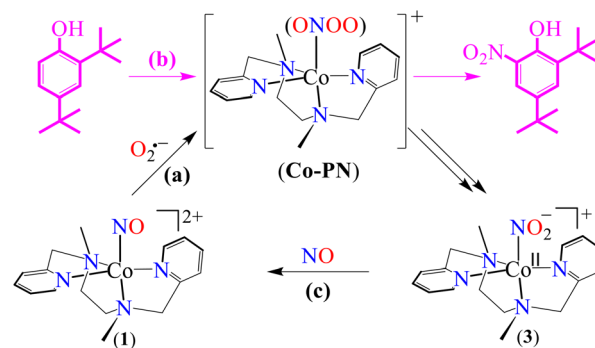


Fig. 3 (a) UV-vis spectral change of **1** (0.25 mM, black line) upon addition of KO₂/18-crown-6 in CH₃CN under Ar at 298 K. Inset: IR spectra of **3**-¹⁴NO₂⁻ (blue line) and **3**-¹⁵NO₂⁻ (red line) in KBr. (b) ESI-MS spectra of **3**. The peak at 375.1 is assigned to [(BPMEN)Co(NO₂⁻)]⁺ (calcd m/z 375.1). Inset: Isotopic distribution patterns of **3**-¹⁴NO₂⁻ (red line) and **3**-¹⁵NO₂⁻ (blue line).



analyses (*vide infra*). The FT-IR spectrum of **3** showed a characteristic peak for Co^{II}-bound NO₂⁻ stretching at 1270 cm⁻¹, which shifted to 1245 cm⁻¹ (¹⁵NO₂⁻) when **3** was generated in the reaction of ¹⁵N-labeled NO {Co¹⁵NO}⁸ and O₂^{•-} (inset: Fig. 3a; ESI, Fig. S6a and b[†]), suggesting that the N-atom in the ¹⁵NO₂⁻ moiety is derived from {Co¹⁵NO}⁸. The ESI-MS spectrum of **3** showed a prominent peak at *m/z* 375.1, [(BPMEN)Co(¹⁴NO₂⁻)]⁺ (calcd *m/z* 375.1), which shifted to 376.1, [(BPMEN)Co(¹⁵NO₂⁻)]⁺ (calcd *m/z* 376.1), when the reaction was performed using {Co¹⁵NO}⁸ (Fig. 3b; ESI, Fig. S7[†]), indicating that the NO₂⁻ derived from the NO moiety of **1**. We did not observe the characteristic signal of aliphatic protons of the BPMEN ligand for **3** in the ¹H-NMR spectrum, signifying a bivalent cobalt center.^{35a,45c} In addition, Evans' method confirmed a low-spin Co^{II}-center (*S* = 1/2), as the magnetic moment of **3** was found to be 1.77 BM (ESI; ES, Fig. S8[†]).⁴⁶ Electrochemical measurement of **3** showed a non-reversible cyclic voltammogram (ESI, Fig. S9[†]). The exact conformation of **3** was determined by single-crystal X-ray crystallographic structural analysis (Fig. 4a, ESI, ES, and Tables T1 and T2[†]). The two NO₂⁻ ligands are coordinated to a Co-center in an end-on fashion with a distorted octahedral geometry. The Co–O–N and O–N–O bond angles were 118.91 and 116.12, respectively. The Griess reagent test confirmed the amount of NO₂⁻ generated in the above reaction and was determined to be 93 (±5)% (ESI; SI, Fig. S10[†]).^{35a,47} Various spectral and structural analyses of **3** undoubtedly showed that the reaction of **1** with O₂^{•-} generated Co^{II}-NO₂⁻ (**3**) as the NOM product (Scheme 1c). The side product of the NOM reaction of **1** was determined to be O₂, which is believed to be formed *via* a proposed transient [Co–PN]⁺ intermediate (Scheme 2). The PN intermediate is known to be a source of the reactive oxygen atom, which can produce O₂;^{35a} also, in an aqueous medium, PN was found to generate the NO₂⁻ anion with O₂.⁴⁸ Recently, one of our reports on the Co^{III}-peroxo reaction with NO showed the generation of NO₂⁻ + O₂ *via* a [Co–PN]⁺ intermediate,²⁴ and similarly Nam and coworkers demonstrated the formation of Co^{II}-NO₂⁻ and O₂ *via* a [Co–PN]⁺ intermediate.^{35a} Likewise, the generation of Cu^{II}-NO₂⁻ with the evolution of O₂ was observed from a [Cu–PN]⁺ intermediate.^{22,49} Hence, in the above reaction, the generation of Co^{II}-NO₂⁻ with O₂ evolution supports our assumption of the proposed [Co–PN]⁺ intermediate, as described in the previous reports on aqueous PN chem-



Scheme 2 Phenol ring nitration to trap the [Co–PN]⁺ intermediate.

istry,⁴⁸ non-aqueous Co^{II}-PN,^{35a} and Cu^{II}-PN^{22,49} chemistry. We followed and trapped the evolved O₂ by following its generation from the reaction solution to support our assumption as proposed in [Co–PN]⁺ chemistry^{19f,20,26} and aqueous PN chemistry.⁴⁸ To confirm the formation of O₂, we carried out the reaction of **1** with O₂^{•-} and followed the generation of gases by reaction flask headspace analysis using a gas-mass analyzer and observed the formation of O₂ (Fig. 4b). In addition, we attempted to characterize the proposed [Co–PN]⁺ intermediate to elucidate the mechanism of its conversion to **3** in the above NOM reaction (Scheme 2). However, our efforts to characterize the [Co–PN]⁺ were futile due to its unstable nature. However, indirectly, the PN intermediate was detected by a DTBP ring-nitration test, as reported in the previous literature^{19c,f,41,42c} and as explained in the chemistry we have described earlier (*vide supra*).¹² The generation of NO₂-2,4-DTBP (~52%) and 2,4-DTBP-D (~12%) (ESI, Fig. S11[†]) actively supports the proposed reaction mechanism in the above NOM reaction and, therefore, the formation of a [Co–PN]⁺ intermediate in the reactions of **1** with O₂^{•-} (Scheme 2, reactions a and b). The formation of a [Co(BPMEN)(NO)(O₂^{•-})]⁺ species before PN formation, as reported earlier, can't be ruled out,^{42c,50} but such an intermediate further undergoes rearrangement to generate the PN intermediate ultimately. We did not observe the formation of such species spectroscopically; however, indirect proof from the phenol ring nitration test confirms the PN formation.

NO oxygenation reaction of the {CrNO}⁵ complex (**2**)

In order to find the influence of the metal center on oxidation of metal-bound nitrosyls, we explored the reaction of [(BPMEN)Cr(NO)(Cl)]⁺ ({CrNO}⁵, **2**) with O₂^{•-} (yield: 70%). Complex **2** was synthesized and isolated by following our previous report.⁴³ The addition of one equivalent of O₂^{•-} (KO₂/18-crown-6) to a CH₃CN solution of **2** under Ar showed a color change from light green to dark red at 298 K. Upon reaction of **2** with O₂^{•-}, the characteristic UV-vis absorption bands of **2** (black line, λ_{max} = 600 nm) changed to a new band (blue line, λ_{max} = 450 nm) within ~one minute (Fig. 5a), which gradually changed to the red line (NO-oxidized product, **4**) in ~five minutes (Fig. 5a, ESI, Fig. S12a[†]) at 298 K under an Ar atmo-

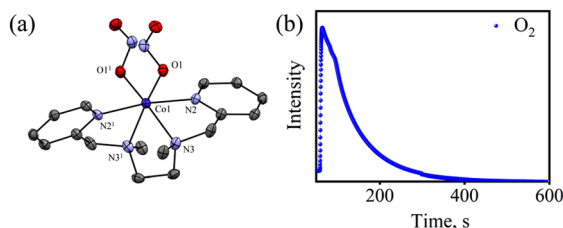


Fig. 4 (a) Displacement ellipsoid plot (30% probability) of **3** at 100 K. H-atoms have been removed for clarity. (b) Mass spectra of the formation of O₂ in the reaction of **1** (20.0 mM) with O₂^{•-}.



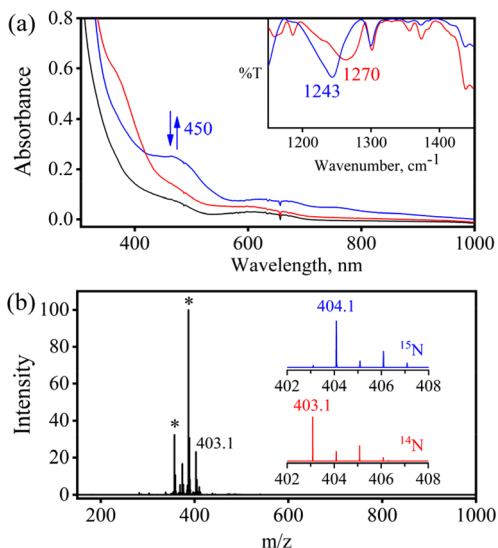


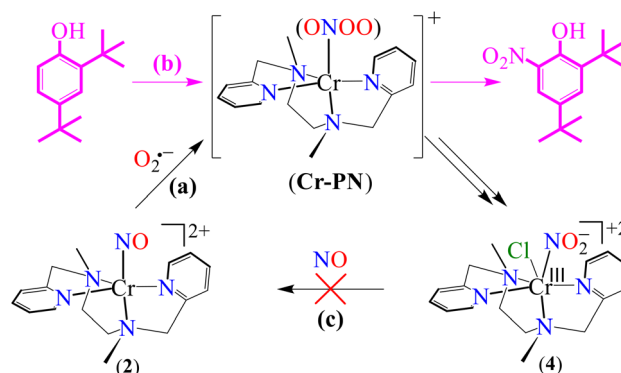
Fig. 5 (a) UV-vis spectral change of **2** (1 mM, black line) upon addition of $\text{KO}_2/18\text{-crown-6}$ showing the formation of the blue line, and it further decomposes to form **4** (red line) in CH_3CN under Ar at 298 K. Inset: IR spectra of $4\text{-}^{14}\text{NO}_2^-$ (red line) and $4\text{-}^{15}\text{NO}_2^-$ (blue line) in KBr. (b) ESI-MS of **4** formed in the reaction of **2** with $\text{KO}_2/18\text{-crown-6}$ recorded in CH_3CN . The peak at m/z 403.1 is assigned to $[(\text{BPMEN})\text{Cr}(^{14}\text{NO}_2^-)(\text{Cl}^-)]^+$ (calcd: m/z 403.1). The peaks at 387.1, 357.1, and 374.1 marked with asterisks are assigned to $[(\text{BPMEN})\text{Cr}(\text{NO})(\text{Cl}^-)]^+$ (calcd: m/z 387.1), $[(\text{BPMEN})\text{Cr}(\text{Cl}^-)]^+$ (calcd: m/z 357.1) and $[(\text{BPMEN})\text{Cr}(\text{OH}^-)(\text{Cl}^-)]^+$ (calcd: m/z 374.1), respectively. Inset: Isotopic distribution patterns of $4\text{-}^{14}\text{NO}_2^-$ (red line) and $4\text{-}^{15}\text{NO}_2^-$ (blue line).

sphere. It is worth noting that **2** does not show any spectral changes in the absence of $\text{O}_2^{\cdot-}$ under similar reaction conditions, suggesting that **2** is thermally stable; therefore, we can rule out the natural decomposition of **2** (ESI, Fig. S12b[†]).⁵¹ In addition to the UV-vis spectral analysis, we investigated the NOO reaction of **2** with different spectral measurements and tried to follow or characterize the proposed $[\text{Cr-PN}]^+$ intermediate. However, being a thermally unstable species, our efforts to spectroscopically characterize the proposed $[\text{Cr-PN}]^+$ failed.

Further, to understand the NOO product of **2**, we characterized the reaction products with different spectral measurements. The FT-IR spectrum of the isolated product (**4**) from the reaction of **2** with $\text{O}_2^{\cdot-}$ showed a new peak at 1270 cm^{-1} , characteristic of NO_2^- stretching frequency (inset in Fig. 5a; ESI, Fig. S13a[†]).^{19b} The NO_2^- stretching frequency shifted to 1243 cm^{-1} ($^{15}\text{N}^{16}\text{O}_2^-$) when reacting ^{15}NO -labeled **2** (i.e., $[(\text{BPMEN})\text{Cr}(^{15}\text{NO})(\text{Cl}^-)]^+$) with $\text{O}_2^{\cdot-}$ (inset in Fig. 5b; ESI, Fig. S13b[†]). The negative shifting of NO_2^- stretching frequency ($\Delta = 27\text{ cm}^{-1}$) denoted that the N atom in the NO_2^- anion came from the NO moiety of **2**. The ESI-MS spectrum of **4** exhibited a prominent ion peak at m/z 403.1, $[(\text{BPMEN})\text{Cr}^{\text{III}}(\text{NO}_2^-)(\text{Cl}^-)]^+$ (calcd. m/z 403.1), which shifted to m/z 404.1, $[(\text{BPMEN})\text{Cr}^{\text{III}}(^{15}\text{NO}_2^-)(\text{Cl}^-)]^+$ (calcd. m/z 404.1), when the reaction was performed with ^{15}N -labeled **2** ($\{\text{Cr}^{15}\text{NO}\}^5$) (Fig. 5b; ESI, Fig. S14[†]), indicating clearly that the NO_2^- in **4** is

derived from the NO moiety. Also, we compared the UV-vis spectrum of **4** with that of independently prepared $\text{Cr}^{\text{III}}\text{-NO}_2^-$ (ESI, Fig. S15[†]), which further confirmed the formation of the $\text{Cr}^{\text{III}}\text{-NO}_2^-$ complex in the NOO reaction of **2**. In addition, we calculated the magnetic moment of **4** by Evans' method and found it to be 3.54 BM (theoretical $\mu_s = 3.87\text{ BM}$), confirming a Cr^{III} center (d^3) (ESI, Fig. S16[†]). Additionally, formation of **4** from the NOM reaction of **2** was also confirmed with EPR spectra as the spectrum of **4** showed a peak at $g = 3.5$ and 4.90 (ESI, Fig. S17[†]).⁵² Cyclic voltammetric measurements of **4** showed a quasi-reversible cyclic voltammogram, clearly different from that of **2**, suggesting a completely new species (ESI, Fig. S16b and c[†]). For the exact validation of the NOO product of **2**, different spectroscopic data of an authentic sample of **4** were compared with those of the product obtained in the reaction of **2** with $\text{O}_2^{\cdot-}$. This comparison confirmed that the oxidized product of **2** is a Cr^{III} -metal complex bound to the NO_2^- anion.^{19b} Complex **4** was found to be thermally stable, showing no natural decay in the UV-Vis measurements (ESI, Fig. S18a[†]). Finally, we determined the amount of NO_2^- ions by a Griess reagent assay^{34a,47} in the reaction of **2** with NO and found it to be 87(\pm 5)% (ESI, Fig. S10[†]). Various spectroscopic characterization studies of **4** showed that the reaction of $\{\text{CrNO}\}^5$ with $\text{O}_2^{\cdot-}$ yielded $\text{Cr}^{\text{III}}\text{-NO}_2^-$ (**4**) as the NOM product (Scheme 3). Using a gas-mass analyzer we observed the formation of O_2 (ESI, Fig. S19b[†]).

Isomerization of the PN moiety is usually possible *via* O–O bond homolysis to form NO_3^- ,^{19c,20,41} or $\text{NO}_2^- + \text{O}_2$ ^{48a,b,53} upon rearrangement. It is known that M–PN intermediates are highly unstable, and there are only a few reports on the spectral characterization of metal-bound PN intermediates.^{19f,20,26–b,54} However, alternatively, PN can also be confirmed using its phenol ring nitration chemistry when reacted with 2,4-DTBP *vide supra*.^{19a–c,f,26b,40b,50a,54a,55} We observed the formation of $\text{NO}_2\text{-2,4-DTBP}$ (yield: 65%) when **2** was reacted with $\text{O}_2^{\cdot-}$ in the presence of 2,4-DTBP (ESI, Fig. S20[†]). This phenol ring nitration test using 2,4-DTBP supports that the reaction of **1** with $\text{O}_2^{\cdot-}$ is going through a proposed $[\text{Cr-PN}]^+$ intermediate and generates $\text{Cr}^{\text{III}}\text{-NO}_2^- + \text{O}_2$ (Scheme 3).



Scheme 3 Phenol ring nitration to trap the $[\text{Cr-PN}]^+$ intermediate.



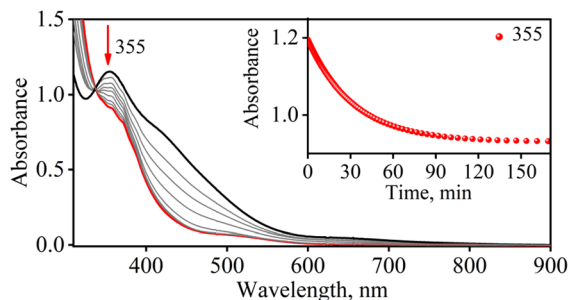


Fig. 6 UV-Vis spectral changes observed in the reaction of **3** (0.5 mM) with NO in CH₃CN under Ar at 233 K. Inset: Time course of decomposition of **3** monitored at 355 nm (red circles).

In addition, to determine the driving forces for the NOO reaction of **1** and **2**, the equilibrium constants (K_{eq}) for the formation of {CoNO}⁸ and {CrNO}⁵ were determined and found to be 88 M⁻¹ and 2270 M⁻¹ (ESI, Fig. S21a and b†), respectively, which suggest that the K_{eq} for **2** is ~25 times larger than that of **1**. This comparison of K_{eq} values undoubtedly suggests that {CrNO}⁵ is more stable than {CoNO}⁸. Hence, the NOO reaction of {CoNO}⁸ was found to be faster than that of {CrNO}⁵ in the presence of O₂^{•-}.

NO activation of NOM products (3 and 4)

To further explore the chemistry of Co^{II}-NO₂⁻ (**3**) and Cr^{III}-NO₂⁻ (**4**) complexes, we investigated their reactions with excess NO. In this regard, we reacted isolated **3** (obtained in the reaction of **1** with one equivalent of O₂^{•-}) with excess NO to explore its NO activation chemistry. In the reaction, we observed the decomposition of the band 355 nm and the formation of a new absorption band ($\lambda_{\text{max}} = 375$ nm) in ~2 hours in CH₃CN under an Ar atmosphere at 233 K, suggesting the generation of a new species, believed to be {CoNO}⁸ (Fig. 6) (Scheme 2, step c). This indicates that complex **1** first reacts with one equivalent of O₂^{•-} to generate the corresponding Co^{II}-NO₂⁻, which reacts further with NO to produce {CoNO}⁸. In contrast to the NO activation of **3**, the reaction of **4** with excess NO did not yield Cr-NO, [(BPMEN)Cr(NO)(Cl)]⁺ (**2**), under similar reaction conditions (Scheme 3, step d and ESI, Fig. S22†) which is so obvious as the end product of the NOO reaction is the Cr^{III} system. The exploration of the NO activation chemistry of Co^{II} (d^7 , $S = 3/2$ or d^7 , $S = 1/2$), Cr^{II} (d^4 , $S = 2$), and Cr^{III} (d^3 , $S = 3/2$) complexes with similar ligand frameworks suggests that M-nitrosyl formation depends on the oxidation states and physical parameters of the metal center.

Conclusion

In this report, we have demonstrated that the nitric oxide oxygenation (NOO) reactions of Co-nitrosyl, [(BPMEN)Co(NO)]²⁺ ({CoNO}⁸, **1**), and Cr-nitrosyl, [(BPMEN)Cr(NO)(Cl)]⁺ ({CrNO}⁵, **2**), complexes, bearing a common BPMEN ligand, are regulated by the stability of metal-nitrosyls and the inter-

mediate species involved in the reactions. Here, we observed that the reaction of **1** with O₂^{•-} generates a Co^{II}-nitrite complex in the same oxidation state, [(BPMEN)Co^{II}(NO₂⁻)₂] (**3**), with O₂ evolution *via* a proposed [Co-PN]⁺ intermediate, as observed in other examples of NOM chemistry.^{22,24} In contrast, when **2** reacted with O₂^{•-}, it generated an oxidized Cr^{III}-nitrite complex, [(BPMEN)Cr^{III}(NO₂⁻Cl)]⁺ (**4**), and O₂ *via* a putative [Cr-PN]⁺ intermediate, similar to the chemistry of Co^{II}-PN and Cu^{II}-PN intermediates.^{22,35a,49a} The proposed PN intermediates in the NOM reaction of **1** and **2** were supported by the phenol ring nitration test. Studies using ¹⁵N-labeled ¹⁵NO revealed that the N-atoms of Co^{II}-NO₂⁻ and Cr^{III}-NO₂⁻ derived from the NO moieties of **1** and **2**, respectively. Both the complexes, **1** and **2**, generate the NOM products (**3** and **4**) when reacted with O₂^{•-}; however, we were only able to regenerate {CoNO}⁸ from **3**, in contrast, {CrNO}⁵ from **4**. In conclusion, the rate of NOM depends on the thermal stability of M-NOs. In contrast, the regeneration of initial M-NOs from NOM products depends on the oxidation states of the metal center of final products.

Conflicts of interest

There are no conflicts to declare.

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