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Reactions of Co(III)–Nitrosyl Complexes with Superoxide and Their Mechanistic Insights

Pankaj Kumar[†], Yong-Min Lee[†], Young Jun Park[†], Maxime A. Siegler[‡], Kenneth D. Karlin^{‡,*}, and Wonwoo Nam^{†,*}

[†]Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea

[‡]Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, United States

Abstract

New Co^{III}-nitrosyl complexes bearing *N*-tetramethylated cyclam (TMC) ligands, [(12-TMC)Co^{III}(NO)]²⁺ (**1**) and [(13-TMC)Co^{III}(NO)]²⁺ (**2**), were synthesized via [(TMC)Co^{II}(CH₃CN)]²⁺ plus NO(g) reactions. Spectroscopic and structural characterization shows that these compounds bind the nitrosyl moiety in a bent end-on fashion. The Co^{III}-nitrosyl complexes, (**1**) and (**2**), reacted with KO₂/2.2.2-Cryptand and produced [(12-TMC)Co^{II}(NO₂)]⁺ (**3**) and [(13-TMC)Co^{II}(NO₂)]⁺ (**4**), respectively; these possess O,O'-chelated nitrito ligands. Mechanistic studies using ¹⁸O-labeled superoxide (¹⁸O₂^{•-}) demonstrate that one oxygen atom in the nitrito ligand derives from superoxide and dioxygen produced comes from the other superoxide oxygen atom. Evidence supporting the formation of a Co-peroxynitrite intermediate is also presented.

Nitric oxide (NO) activation by transition metal ions has attracted enormous interest from chemists and biochemists, since NO has been discovered to play major roles in many biophysiological processes, such as vascular regulation, neurotransmission and immune cytotoxicity.¹ In this context, the biosynthesis of NO and its various biological and physiological reactivities come about through the interaction with metalloproteins of iron and/or copper.² However, NO overproduction leads to toxicological behavior because of its radical character and ability to form reactive nitrogen species (RNS), such as nitrogen dioxide (NO₂) and peroxynitrite (PN, ⁻OON=O).³ These RNS may result from NO oxidation in the presence of O₂,⁴ H₂O₂, superoxide radical^{3d,5} and/or transition metal ions.⁶ In these contexts, important enzymes are available *in-vivo* to maintain proper levels of NO. For example, detoxification by removal of NO occurs by nitric oxide dioxygenases (NODs), which are microbial or mammalian heme proteins.^{2d,7} The chemistry here involves reactions of oxy-hemes (e.g., iron(III)-superoxo species) with NO to generate biologically benign nitrate ion (NO₃⁻), and this process is believed to occur through the formation of metal-peroxynitrite (PN) intermediates.

*Corresponding Author. karlin@jhu.edu; wwnam@ewha.ac.kr.

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The coordination chemistry of metal-nitrosyl complexes has a long history^{7b,8} including a significant literature wherein these are exposed to oxidants such as O₂.⁹ Clarkson and Basolo first described the chemistry of a cobalt-nitrosyl complex with O₂, in which oxygenation leads to a nitrite-bound product.^{9a,9b} In other examples, a nonheme dinitrosyl-iron complex reacts with O₂ to give nitrate,^{10a} whereas a copper-NO species gives a Cu-PN intermediate which transforms to nitrite and O₂.^{10b} Recently, Mondal and coworkers reported the reactivity of Cu-NO complex with H₂O₂, forming a copper-nitrato complex via the thermal decomposition of a presumed Cu^I-PN intermediate.¹¹

Further, there are recent chemistries associated with metal-oxygen coordination complexes with NO. In such biomimetic studies, mononuclear metal-superoxo species have been shown to react with NO to produce metal-PN (Mⁿ⁺-OON=O) intermediates, including examples with heme, non-heme Fe, Co or Cu.¹² For example, we reported recently the conversion of a non-heme Cr^{IV}-peroxo complex to a Cr^{III}-nitrate ion upon addition of NO,^{13a} whereas the reaction of a Cr^{III}-superoxo complex with NO gave a high-valent Cr^{IV}-oxo species and nitrogen dioxide (NO₂) via the formation of a presumed Cr^{III}-PN intermediate.^{13b} Thus, a variety of outcomes can occur when metal complexes in varying oxidation states mediate reactions of NO (or NO⁺) with differing reduced O₂-derivatives (e.g., superoxide or peroxide). Included is the capture of a peroxyxynitrite (or NO₂) intermediate via nitration of added phenols, which is analogous to biologically well established tyrosine nitration which effects biomolecule damage or participates in cellular signalling events.^{3a,b,6,14}

Herein, we report the synthesis, characterization and superoxide reactivity of Co^{III}-nitrosyl complexes bearing 12- and 13-membered TMC ligands, [(12-TMC)Co^{III}(NO)]²⁺ (**1**, 12-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) and [(13-TMC)Co^{III}(NO)]²⁺ (**2**, 13-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane) (Scheme 1, reactions I and II). These Co^{III}-nitrosyl complexes do not show a reactivity toward dioxygen (O₂) (Scheme 1, reaction II) but react with superoxide anion (O₂^{•−}) to form their corresponding Co^{II}-nitrito complexes, [(12-TMC)Co^{II}(NO₂)]⁺ (**3**) and [(13-TMC)Co^{II}(NO₂)]⁺ (**4**), and O₂ via the formation of presumed Co^{II}-PN intermediates (Scheme 1, reactions III and IV). Mechanistic studies using ¹⁸O-labeled superoxide (¹⁸O₂^{•−}) demonstrate unambiguously that one O-atom in the nitrito ligand derives from the superoxide anion and the other O-atom of the superoxide is used to form O₂ (Scheme 1). To the best of our knowledge, this study reports the first mechanistic investigation of the reaction of metal-NO complexes with superoxide and the first clear evidence showing that O-O bond formation to evolve O₂ occurs in this type of metal-NO oxidative chemistry.

Addition of excess NO(g) to the solutions of cobalt(II) complexes, [(12-TMC)Co^{II}(NCCH₃)]²⁺ and [(13-TMC)Co^{II}(NCCH₃)]²⁺, in CH₃CN at −40 °C under an Ar atmosphere resulted in the generation of **1** and **2** within 1 min, respectively (Scheme I, reaction I; also see Supporting Information (SI), Experimental Section and Figure S1 for a schematic diagram of the NO(g) purification and handling process). UV-vis spectra of **1** and **2** exhibit characteristic absorption bands at 368 nm (ε = 950 M^{−1} cm^{−1}) and 375 nm (ε = 750 M^{−1} cm^{−1}), respectively (Figure 1; also see SI, Figures S2 and S3 for the UV-vis spectral changes). Electron paramagnetic resonance (EPR) spectra recorded for **1** and **2** are silent, suggesting the trivalency of the cobalt center (SI, Figure S4; see also Figure S5 for ¹H

NMR) and thus formally $\text{Co}^{\text{III}}(\text{NO}^-)$ or $\{\text{Co}(\text{NO})\}^8$ descriptions (vide infra).⁸ Solution IR spectra of **1** and **2** are also consistent with these formulations, revealing low energy (for $\{\text{Co}(\text{NO})\}^8$) NO stretching bands at 1712 cm^{-1} and 1716 cm^{-1} , respectively (SI, Figures S6 and S7).⁸ Electrospray ionization mass spectra (ESI-MS) recorded for **1** and **2** show prominent ion peaks at $m/z = 416.1$ and 430.1 , respectively (Figure 1, insets), whose mass and isotope distribution pattern correspond to $[(12\text{-TMC})\text{Co}(\text{NO})(\text{ClO}_4)]^+$ (calc. m/z 416.1) and $[(13\text{-TMC})\text{Co}(\text{NO})(\text{ClO}_4)]^+$ (calc. m/z 430.1), (SI, Figures S8 and S9).

In addition to the above spectroscopic characterization, **1** and **2** were structurally characterized via single crystal X-ray crystallography. In both structures, perchlorate are used as counter anions, and the molecular formulas for both compounds are $[(12\text{-TMC})\text{Co}^{\text{III}}(\text{NO})](\text{ClO}_4)_2$ **1** and $[(13\text{-TMC})\text{Co}^{\text{III}}(\text{NO})](\text{ClO}_4)_2$ **2** (Figure 2; SI, Tables S1 and S2). In both structures, the NO ligand is axially coordinated to the cobalt centre in an end-on fashion with a distorted square pyramidal geometry for cobalt(III), and all four TMC *N*-methyl groups are pointed *syn* to the NO moiety. The N(5)-O(1) bond length in **1** and **2** are statistically identical ($1.155(2)\text{ \AA}$ in **1** and $1.159(5)\text{ \AA}$ in **2**). The large bending of the metal-nitrosyl moiety, with Co(1)-N(5)-O(1) bond angles of $128.50(13)^\circ$ for **1** and $124.4(3)^\circ$ for **2**, is also consistent with the coordinated NO^- ,⁸ thus further consistent with our assignment of these complexes as $\text{Co}^{\text{III}}(\text{NO}^-)$ species.

To further elaborate the chemistry of **1** and **2**, we explored their reactions with oxidants, such as dioxygen (O_2) and superoxide ($\text{O}_2^{\bullet-}$). Both Co^{III} -nitrosyl complexes, **1** and **2**, were found to be inert toward O_2 (Scheme 1, reaction II), in stark contrast to the previously studied cobalt complexes.^{8,9} We speculate that for **1** and **2**, there is absolutely no NO dissociation, which may be required to lead to O_2 reactivity.^{7b} However, they do exhibit $\text{O}_2^{\bullet-}$ reactivity, as with KO_2 in CH_3CN with 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane (2.2.2-cryptand), gives corresponding Co^{II} -nitrito complexes (Scheme 1, reactions III and IV). When **1** was reacted with 1 equiv of $\text{O}_2^{\bullet-}$ in the presence of 2.2.2-cryptand under Ar atmosphere in CH_3CN at $-10\text{ }^\circ\text{C}$, the color of the reaction solution was changed from dark to a very light pink (SI, Experimental Section) to form new species (**3**); the characteristic absorption band at 368 nm for **1** disappeared within 2 min (Figure 3; also see SI, Figure S10). Similarly, **2** reacted with 1 equiv of $\text{O}_2^{\bullet-}$ (SI, Figure S11 for UV-vis spectral changes) to form the product (**4**). Spectral titration data clearly showed that the stoichiometric ratios for both reactions of **1** and **2** with $\text{O}_2^{\bullet-}$ were 1:1 (see SI, Figure S12). The products **3** and **4** obtained in the reactions of **1** and **2** with $\text{O}_2^{\bullet-}$, respectively, were determined to be Co^{II} -nitrito complexes on the basis of spectroscopic and structural characterization using solution IR, EPR, and ESI-MS spectroscopies and single crystal X-ray crystallography (vide infra).¹⁵ The yields of the Co^{II} -nitrito products, **3** and **4** ($85 \pm 4\%$ and $83 \pm 4\%$, respectively) were determined by nitrite ion analyses, either using Quantofix test strips or the Griess reagent (see SI, Experimental Section and Figure S13).

The reaction of **1** with 1 equiv of $\text{O}_2^{\bullet-}$ in CH_3CN at $-40\text{ }^\circ\text{C}$ was followed by solution IR spectroscopy (Figure 3, inset); the NO stretching vibration at 1712 cm^{-1} decreases with simultaneous growth of new peaks at 1261 and 1300 cm^{-1} due to **3**, which are assignable to NO_2^- vibrational signals. Similar solution IR spectral changes were observed in the reaction of **2** and $\text{O}_2^{\bullet-}$ (SI, Figure S11a, inset), indicating that NO_2^- complex, **4**, was generated. EPR

spectra of **3** and **4** exhibit signals at $g = 5.8, 4.3$ and 2.16 for **3** and $g = 5.9, 3.3$ and 2.16 for **4**, which are indicative of d^7 high-spin ($S = 3/2$) Co(II) species (SI, Figures S14a and S14b).

Absolute confirmation of the Co^{II}-nitrito complexes, **3** and **4**, comes from the X-ray crystallographic analysis (Figure 4). The [(12-TMC)Co^{II}(η^2 -O₂N)]⁺ (**3**) and [(13-TMC)Co^{II}(η^2 -O₂N)]⁺ (**4**) complexes possess O,O'-chelated bidentate nitrito ligands, thus giving overall six-coordinate distorted octahedral Co(II) complexes (see SI for experimental and structural details; see also Tables S3 and S4). For **3**, there are two crystallographically independent formula units (i.e., $Z' = 2$) with almost identical chemical conformation in the asymmetric unit whereas $Z' = 1$ for **4**. In both **3** and **4**, the difference of the two Co-O bond distances is within $0.02 \text{ \AA}$, reflecting a very minimal Jahn-Teller distortion, which is also consistent with the observed IR spectroscopic properties, showing that the differences between two N-O vibrational signals for **3** and **4** are 39 cm^{-1} and 40 cm^{-1} , respectively. These differences in vibrational signals are much smaller than that found in the case of asymmetric binding of NO₂⁻ to metal center.¹⁶

ESI-MS was also employed to analyze the source of oxygen atoms in NO₂⁻ ligand for **3** (Figure 5a) and **4** (SI, Figure S15a). The peak at m/z 333.1 in Figure 5a corresponds to [(12-TMC)Co(NO₂)]⁺ (calc. m/z 333.2). We then analyzed **3** prepared using ¹⁸O-labeled K¹⁸O₂ to track the oxygen source in NO₂⁻ ligand (SI, Experimental Section); the peak at m/z 335.1 is assigned to [(12-TMC)Co^{II}(N¹⁶O¹⁸O)]⁺ (calc. m/z 335.2) (Figure 5a, inset). The observation of the two mass unit shift from m/z 333.1 to 335.1 in this reaction indicates that one of the two O-atoms in NO₂⁻ ligand of **3** derives from superoxide anion (vide infra).

The supposition that the formation of Co^{II}-nitrito complex would be accompanied by release of dioxygen (Scheme 1, reaction IV) comes from both (i) the literature^{17,18} on aqueous peroxyxynitrite chemistry where HOON=O + ⁻OON=O react to give 2NO₂⁻ + O₂ + H⁺ and (ii) examples where Cu^{II}-peroxyxynitrite complexes transformed to Cu^{II}-nitrito plus dioxygen.^{10b,12c,15} Both (i) and (ii) involve the initial formation of peroxyxynitrite species, and mechanistic considerations are discussed further below.

As mentioned in the introductory material, metal-peroxyxynitrite complexes may be formed from a variety of reaction types. Here, for the first time, we have described the reaction of a metal-nitrosyl complex with superoxide anion. In this reaction, we propose that in the first step, O₂^{•-} directly adds to the NO moiety in [(12-TMC)Co^{III}(NO)]²⁺ (**1**) (or [(13-TMC)Co^{III}(NO)]²⁺ (**2**)), giving a transient Co^{II}-PN species which comes about by an internal electron-transfer to Co^{III} (Scheme 1, reaction III). Following mechanisms earlier proposed for PN_(aq) chemistry involving initial O-O homolytic cleavage,^{3d} and also applied to Cu²⁺_(aq)¹⁵ and non-aqueous copper complex chemistry,^{10b,12c} the sequence of reactions shown in Scheme 2 will lead to the products observed (see also SI, Figure S15b for ESI-MS), including a half ¹⁸O-labeled nitrite moiety and ¹⁸O₂. Detection of dioxygen in significant amounts, by reaction flask head-space analysis using mass spectrometry (see SI, Experimental Section), indeed shows that only ¹⁸O₂ is formed in the reaction of **1** and ¹⁸O-labeled superoxide (¹⁸O₂^{•-}) (Figure 5b). This result was also confirmed by carrying out a reaction using ¹⁶O₂^{•-}/¹⁸O₂^{•-} (1:1) superoxide mixture, in which a significant amount of ¹⁶O-¹⁸O molecules was formed along with the formation of ¹⁶O-¹⁶O and ¹⁸O-¹⁸O

molecules (Figure 5b, inset). Notably, this finding is exactly consistent with the proposed mechanism in Scheme 2, with initial O–O homolytic cleavage and then involving O–O bond formation (Scheme 2, steps 1 and 2).¹⁸ This is the first example in which tracking of the oxygen atoms reveals that the O₂ produced does indeed derive from the PN peroxidic moiety (here derived from O₂^{•-}), as proposed for aqueous PN chemistry.^{17,18}

While we do not have direct spectroscopic evidence for the postulated Co^{II}-PN species, support for its formation comes from our finding that it can be intercepted by addition of a phenolic substrate, here 2,4-di-*tert*-butylphenol to produce 2,4-di-*tert*-butyl-6-nitrophenol in good yields(>50%) with oxidative coupling occurring to most of the remaining phenol substrate (see SI, Experimental Section). It should be noted that phenol nitration has been used extensively to provide evidence for the presence of metal-peroxynitrite species,^{3a,3b,6a,14} and as mentioned, this reaction is of considerable biological importance. It is also noted that Co-NO complexes, **1** and **2**, do not react with the phenol.

In summary, we synthesized two mononuclear Co^{III}-nitrosyl complexes, [(12-TMC)Co^{III}(NO)]²⁺ (**1**) and [(13-TMC)Co^{III}(NO)]²⁺ (**2**), and examined their reactions with O₂ and O₂^{•-} (Scheme 1). The Co^{III}-nitrosyl complexes were inert toward O₂, but for this very new reaction type, reacted with superoxide cleanly to give high yields of Co^{II}-nitrito complexes with the release of dioxygen via the formation of presumed Co-PN intermediates. It is worth noting that the O₂ evolution does involve a rather unique kind of O–O bond forming process, as otherwise discussed in O₂-evolving enzymatic reactions, such as Photosystem II (PS II) and chlorite dismutase (Cld).¹⁹ The present results add to the only very few examples of metal-peroxynitrite species involving nitrite plus O₂ product formation, while new mechanistic insights have been added.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

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 18. The present formation of $^{16}\text{O}-^{18}\text{O}$ dioxygen is *not* consistent with two PN molecules reacting in a 'peracid' type mechanism (but now with two Co-PN complexes interacting), where such $\text{PN}_{(\text{aq})}$ solutions give $2\text{NO}_2^- + \text{O}_2$.^{17c,d} For this 'peracid' mechanism and employing $^{16}\text{O}_2^{\bullet-}/^{18}\text{O}_2^{\bullet-}$ (1:1) superoxide mixtures, only $^{16}\text{O}_2$ or $^{18}\text{O}_2$ should form, since molecular oxygen derives from $^-\text{OO}-\text{NO}_2$ cleavage from an intermediate peroxyxynitrate ($^-\text{OONO}_2$) species which would form.^{5,17c,d}

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Figure 1.

(a) UV-vis spectra of $[(12\text{-TMC})\text{Co}^{\text{II}}(\text{MeCN})]^{2+}$ (0.50 mM, black line) and **1** (red line).

Inset shows the ESI-MS spectrum of **1**. (b) UV-vis spectra of $[(13\text{-TMC})\text{Co}^{\text{II}}(\text{MeCN})]^{2+}$ (0.50 mM) and **2** (red line). Inset shows the ESI-MS spectrum of **2**.

Figure 2. Displacement ellipsoid plots (50 % probability level) of (a) [(12-TMC)Co^{III}(NO)]²⁺ (**1**) and (b) [(13-TMC)Co^{III}(NO)]²⁺ (**2**) at 100 K. Disorder, and the H atoms have been removed for clarity. Gray, C; blue, N; red, O; dark blue, Co. See SI, Tables S1 and S2 for crystallographic and structural data.

Figure 3.

UV-vis spectral changes of **1** (0.50 mM; red line) upon addition of 1 equiv of KO₂/2.2.2-cryptand under Ar atmosphere in CH₃CN at -10 °C. The final blue line for **3** was generated within 2 min. Insets show the solution IR spectral changes of **1** (3.0 mM; red lines) upon addition of 1 equiv KO₂/2.2.2-cryptand under Ar atmosphere in CH₃CN at -40 °C. The final blue line for **3** was generated within 0.5 h.

Figure 4.

Displacement ellipsoid plots (50% probability level) of (a) $[(12\text{-TMC})\text{Co}^{\text{II}}(\eta^2\text{-O}_2\text{N})]^+$ (**3**) and (b) $[(13\text{-TMC})\text{Co}^{\text{II}}(\eta^2\text{-O}_2\text{N})]^+$ (**4**) at 100 K. H atoms have been omitted for clarity.

Gray, C; blue, N; red, O; dark blue, Co. Crystallographic data and selected bond lengths (Å) and angles (°) for **3** and **4** are summarized in SI, Tables S3 and S4.

Figure 5.

(a) ESI-MS spectrum of **3**. Peak at $m/z = 333.1$ is assigned to $[(12\text{-TMC})\text{Co}^{\text{II}}(\text{NO}_2)]^+$ (calc. $m/z = 333.2$). Insets show the isotope distribution patterns for **3**- $^{16}\text{O}^{16}\text{O}$ (blue line) and **3**- $^{16}\text{O}^{18}\text{O}$ (red line). (b) Mass spectra of O_2 isotopes, 32 (^{16}O - ^{16}O ; blue circles), 34 (^{16}O - ^{18}O ; black squares), and 36 (^{18}O - ^{18}O ; red triangles), produced in the reaction of **1** (2.0 mM) with ^{18}O -labeled $\text{K}^{18}\text{O}_2/2.2.2\text{-cryptand}$ (2.0 mM) in CH_3CN at -40°C . Inset shows mass spectra of O_2 isotopes produced using 1:1 mixture of $\text{K}^{16}\text{O}_2/\text{K}^{18}\text{O}_2$ (2.0 mM) in the reaction of **1** (2.0 mM).

Scheme 1.

Scheme 2.