

Chromium(IV)–Peroxo Complex Formation and Its Nitric Oxide Dioxygenase Reactivity

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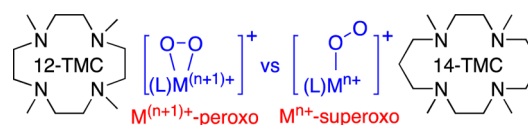
Supporting Information

ABSTRACT: The O₂ and NO reactivity of a Cr(II) complex bearing a 12-membered tetraazamacrocyclic *N*-tetramethylated cyclam (TMC) ligand, [Cr^{II}(12-TMC)(Cl)]⁺ (**1**), and the NO reactivity of its peroxo derivative, [Cr^{IV}(12-TMC)(O₂)(Cl)]⁺ (**2**), are described. By contrast to the previously reported Cr(III)–superoxo complex, [Cr^{III}(14-TMC)(O₂)(Cl)]⁺, the Cr(IV)–peroxo complex **2** is formed in the reaction of **1** and O₂. Full spectroscopic and X-ray analysis revealed that **2** possesses side-on η²-peroxo ligation. The quantitative reaction of **2** with NO affords a reduction in Cr oxidation state, producing a Cr(III)–nitrate complex, [Cr^{III}(12-TMC)(NO₃)(Cl)]⁺ (**3**). The latter is suggested to form via a Cr(III)–peroxynitrite intermediate. [Cr^{II}(12-TMC)(NO)(Cl)]⁺ (**4**), a Cr(II)–nitrosyl complex derived from **1** and NO, could also be synthesized; however, it does not react with O₂.

Mononuclear metal–dioxygen (M–O₂) species, such as metal–peroxo and –superoxo complexes, are critical components of processes leading to practical substrate oxidative transformations.¹ They have also been invoked as key intermediates in enzymatic reactions incorporating oxygen atoms into newly biosynthesized molecules as well as in the deleterious reactions of biological oxidative stress and enzymatic detoxification reactions of reactive oxygen species.² In biomimetic studies, synthetic analogues of M–O₂ intermediates have been intensively investigated to understand factors that control their geometric and electronic properties and chemical reactivity to form related active oxygen species or effect substrate oxidations.³

Recently, metal complexes with O₂-derived ligands and bearing *N*-tetramethylated cyclam (TMC)⁴ chelates have been the subject of intense scrutiny.^{5–8} In these studies, it has been demonstrated that the nature of the supporting TMC ligand plays important roles in regulating the stability, geometric and electronic structure, and reactivity of the dioxygen or reduced derivatives in M–O₂ complexes. One notable example is the finding that [Ni(O₂)(*n*-TMC)]⁺ complexes vary depending on the ring size of the TMC ligand; a side-on Ni(III)–peroxo complex is formed with 12-TMC,⁹ whereas a 14-TMC ligand⁹ affords an end-on Ni(II)–superoxo complex (Scheme 1).⁶

Scheme 1



These results demonstrate that the supporting TMC ligand modulates not only the binding mode of the O₂ ligand (e.g., an end-on superoxo vs a side-on peroxo) but also the preferred oxidation state of the Ni ion (e.g., Ni²⁺ vs Ni³⁺).

Metal ion/nitric oxide (NO) interactions are of great interest, since NO plays important roles in physiological processes, including as a signaling agent and in mammalian immune response.¹⁰ However, overproduction of NO can lead to toxicological processes via the formation of reactive nitrogen species (RNS), including NO₂ and peroxynitrite. One manner in which proper NO levels are maintained is when microbial or mammalian heme protein NO dioxygenases [including hemoglobins (Hbs)] mediate the reaction of O₂ (via Fe^{III}–superoxo species) and NO to yield the biologically benign NO₃[−] ion.^{11,12} In biomimetic studies, mononuclear M–O₂ complexes, best described as metal–superoxo species, have recently been shown to react with NO, giving peroxynitrite (“OON=O; “normally” formed from NO plus O₂^{•−})^{11,13} species or chemistry.^{14–16} However, the reaction of NO with metal–peroxo intermediates has rarely been investigated.

Here we report the synthesis, spectroscopic characterization, and crystal structure of a side-on Cr(IV)–peroxo complex bearing a 12-TMC ligand, [Cr^{IV}(12-TMC)(O₂)(Cl)]⁺ (**2**); the crystal structure of an end-on Cr(III)–superoxo complex bearing a 14-TMC ligand, [Cr^{III}(14-TMC)(O₂)(Cl)]⁺,⁷ was reported previously (see Scheme 1). We also describe the NO dioxygenase chemistry of Cr(IV)–peroxo complex **2**, in which a Cr(III)–nitrate complex, [Cr^{III}(12-TMC)(NO₃)(Cl)]⁺ (**3**), is formed quantitatively.

The starting material, [Cr^{II}(12-TMC)(Cl)]⁺ (**1**), was synthesized by reacting CrCl₂ with the 12-TMC ligand in CH₃CN under Ar [see the Experimental Section, Figure S2, and Tables S1 and S2 in the Supporting Information (SI)]. Bubbling O₂ through a blue solution of **1** in CH₃CN at −20 °C

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produced a purple intermediate **2**, which persisted for several days at room temperature. The UV–vis spectrum of **2** shows a distinct absorption band at 532 nm ($\epsilon = 310 \text{ M}^{-1} \text{ cm}^{-1}$; Figure 1a). Electrospray ionization mass spectrometry (ESI-MS) of **2**

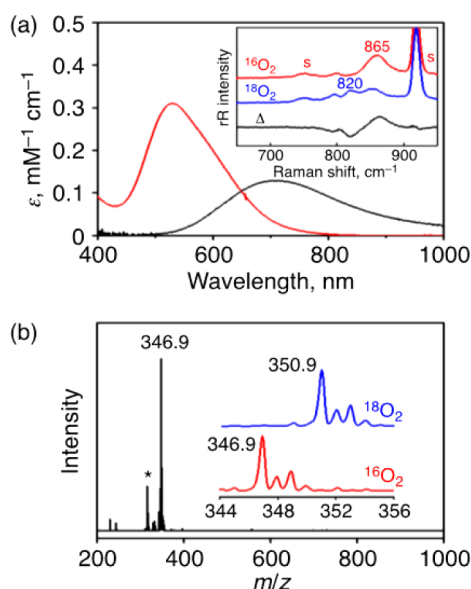


Figure 1. (a) UV–vis spectra of **1** (black) and **2** (red) in CH_3CN at 0°C . Inset: rR spectra of **2** prepared with $^{16}\text{O}_2$ (red) and $^{18}\text{O}_2$ (blue) and the difference spectrum (black). (b) ESI-MS spectrum of **2**. The peak at m/z 315.3 labeled with an asterisk was assigned to $[\text{Cr}^{\text{II}}(12\text{-TMC})(\text{Cl})]^+$ (calcd m/z 315.1). Inset: isotope distribution patterns for **2**- ^{16}O (red) and **2**- ^{18}O (blue).

(Figure 1b) revealed a prominent ion peak at m/z 346.9 whose mass and isotope distribution pattern correspond to $[\text{Cr}(12\text{-TMC})(\text{O}_2)(\text{Cl})]^+$ (calcd m/z 347.1). When the reaction was carried out with isotopically labeled $^{18}\text{O}_2$, a peak corresponding to $[\text{Cr}(12\text{-TMC})(^{18}\text{O}_2)(\text{Cl})]^+$ (**2**- ^{18}O) appeared at m/z 350.9 (calcd m/z 351.1) (Figure 1b inset). The observation of an increase of m/z 4 upon substitution of ^{16}O with ^{18}O indicates that **2** contains an O_2 unit. The resonance Raman (rR) spectrum of **2** was collected using 407 nm excitation in CH_3CN at -20°C . The sample of **2** prepared with $^{16}\text{O}_2$ exhibited an isotope-sensitive band at 865 cm^{-1} that shifted to 820 cm^{-1} when **2** was prepared with $^{18}\text{O}_2$, consistent with its assignment as an O–O peroxide stretching vibration.¹⁷ This assignment could also be made on the basis of the $^{16}\Delta - ^{18}\Delta$ value of 45 cm^{-1} (Figure 1a inset; calcd $^{16}\Delta - ^{18}\Delta = 49 \text{ cm}^{-1}$), which is comparable to those recorded for spectroscopically and structurally characterized side-on metal–peroxo complexes bearing TMC ligands, such as $[\text{Fe}(14\text{-TMC})(\text{O}_2)]^+$ (825 cm^{-1}),^{8a} $[\text{Co}(12\text{-TMC})(\text{O}_2)]^+$ (902 cm^{-1}),^{8b} and $[\text{Ni}(12\text{-TMC})(\text{O}_2)]^+$ (1002 cm^{-1}).^{6b} Moreover, **2** in CH_3CN at 5 K exhibited a silent electron paramagnetic resonance (EPR) spectrum, consistent with the tetravalency assigned to the Cr ion in **2**.

The X-ray crystal structure of **2** revealed that the Cr center is situated in a seven-coordinate environment with the 12-TMC ligand, O_2 , and an aqua ligand (Figure 2a). It was found that the aqua ligand coordinates to the Cr center and the two chloride anions exist as counteranions in the crystal packing, giving a crystal formula of $[\text{Cr}(12\text{-TMC})(\text{O}_2)(\text{OH}_2)]\text{Cl}_2$ (**2'** $\cdot\text{Cl}_2$), although the chloride ligand was found within the formula of **2** in the ESI-MS measurements.¹⁸ Notably, the O–O moiety

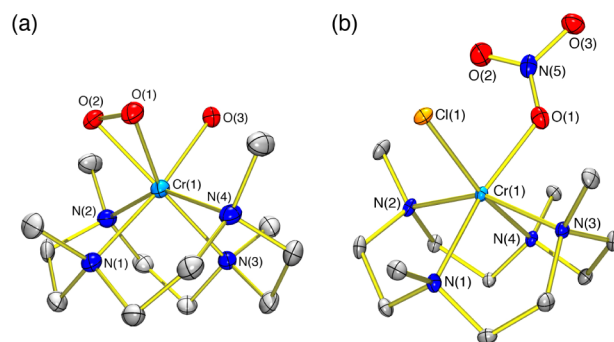


Figure 2. ORTEP diagrams of (a) $[\text{Cr}^{\text{IV}}(12\text{-TMC})(\text{O}_2)(\text{OH}_2)]^{2+}$ (**2'**) and (b) $[\text{Cr}^{\text{III}}(12\text{-TMC})(\text{NO}_3)(\text{Cl})]^+$ (**3**) with 30% probability thermal ellipsoids. H atoms have been omitted for clarity. Gray, C; blue, N; red, O; sky blue, Cr; orange, Cl. Crystallographic data and selected bond distances (\AA) and angles (deg) for **2'** $\cdot\text{Cl}_2$ and **3** are summarized in Tables S1–S4.

was found to be bound to the Cr center in a side-on manner, and the O–O bond length in **2'** (1.394 \AA) is longer than that in the end-on Cr(III)–superoxo complex $[\text{Cr}^{\text{III}}(14\text{-TMC})(\text{O}_2)(\text{Cl})]^+$ (1.231 \AA).^{7a} **2'** should be categorized as a metal–peroxo complex (O–O = ~ 1.4 – 1.5 \AA) rather than a metal–superoxo complex (O–O = ~ 1.2 – 1.3 \AA).^{17,19} The O–O bond length in **2'** is short; however, a similar O–O bond distance of 1.386 \AA was found for a related nickel–peroxo complex, $[\text{Ni}^{\text{III}}(12\text{-TMC})(\text{O}_2)]^+$.^{6b} In **2'**, all four N-methyl groups are pointed *syn* to the peroxo moiety, whereas those in the Cr–superoxo complex $[\text{Cr}^{\text{III}}(14\text{-TMC})(\text{O}_2)(\text{Cl})]^+$ are oriented *anti* to the superoxo moiety.^{7a}

To elaborate further the chemistry of $[\text{Cr}^{\text{IV}}(12\text{-TMC})(\text{O}_2)(\text{Cl})]^+$ (**2**), we reacted it with $\text{NO}(\text{g})$. Complex **2** in CH_3CN (2 mM) was bubbled with Ar for 30 min at 0°C , and an excess amount of NO was then added over the top of this solution. The observed UV–vis spectral changes revealed isosbestic points at 383, 447, and 605 nm (Figure 3a). In an ESI-MS measurement, the peak cluster centered at m/z 377.0 was assigned to a Cr(III)–nitrate complex formulated as $[\text{Cr}^{\text{III}}(12\text{-TMC})(\text{NO}_3)(\text{Cl})]^+$ (**3**) (calcd m/z 377.1) (Figure 3b). The EPR spectrum of **3** revealed signals expected of a d^3 Cr(III) ion ($S = 3/2$) (Figure S3).²⁰ Furthermore, the X-ray crystal structure of **3** revealed that the nitrate anion coordinates to the chromium center bearing the 12-TMC ligand, giving a six-coordinate configuration (Figure 2b).²¹

The yield of the reaction was quantitative on the basis of the UV–vis spectral changes and the absorptivity of authentic complex **3** at 415 nm ($\epsilon = 180 \text{ M}^{-1} \text{ cm}^{-1}$).²² According to the results, we propose the reaction mechanism shown in Scheme 2. As in the generally accepted course of reactions of Fe(III)–superoxo species with NO by Hbs,^{11,12b} the first step should be nucleophilic attack of $[\text{Cr}^{\text{IV}}(\text{O}_2)(12\text{-TMC})(\text{Cl})]^+$ (**2**) on NO. As the Cr–peroxo species has an O_2 fragment that is further reduced by one electron (i.e., with peroxo character), the formation of a Cr–peroxynitrite intermediate would result in metal reduction, giving a $\text{Cr}^{\text{III}}-(\text{OON}=\text{O}^-)$ species (Scheme 2, step a). Although we have proposed the reaction between the Cr(IV)–peroxo species and NO, we cannot rule out the presence of an undetectable equilibrium between Cr(IV)–peroxo and Cr(III)–superoxo species in solution, with the latter, present in tiny amounts, being the species that reacts with NO to give the Cr(III)–peroxynitrite intermediate. Qualitatively, we observed that increased amounts of NO led

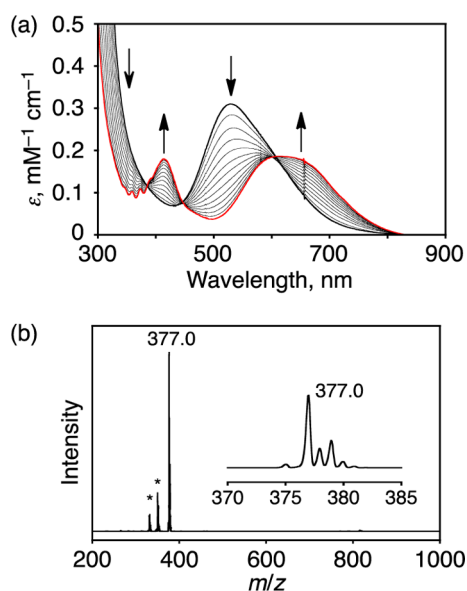
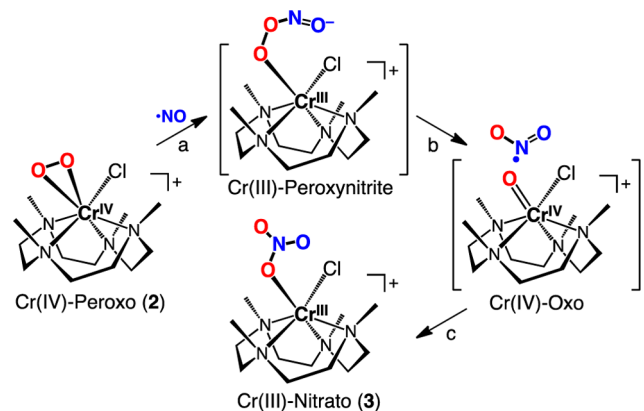


Figure 3. (a) UV-vis spectral changes of **2** (2 mM) upon addition of NO(g) (10 cm³, ~1 atm) into the headspace above a solution of **2** in CH₃CN at 0 °C under Ar (**2**, black line; **3**, red line). (b) ESI-MS spectrum of **3**. Inset: isotope distribution pattern for **3** at *m/z* 377.1. The peaks at *m/z* 350.1 and 332.1 labeled with asterisks were assigned to [Cr^{III}(12-TMC)(Cl₂)⁺] and [Cr^{III}(12-TMC)(OH)(Cl)]⁺, respectively.

Scheme 2

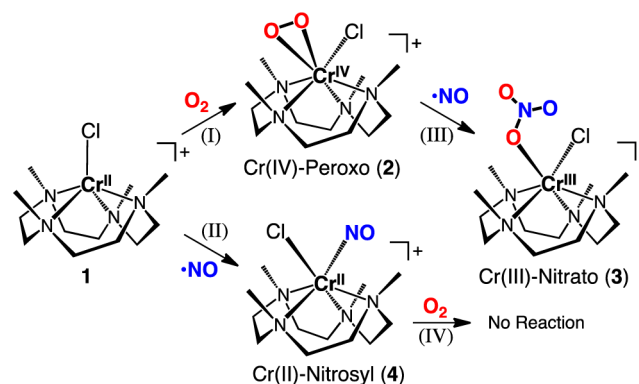


to faster reactions, suggesting the direct interaction of nitric oxide with **2**. Subsequent homolytic O–O bond cleavage of the peroxynitrite moiety would form a Cr(IV)–oxo species and NO₂ (Scheme 2, step b); as suggested for many examples,^{10b,11,23c} the latter would rebind to the Cr(IV)–oxo species to form the observed Cr(III)–nitrate complex (Scheme 2, step c). The lifetime of such a metal-bound peroxynitrite species is expected to be extremely short.²³ The one metal–peroxynitrite complex that has been isolated is [Co(CN)₅(OONO)]³⁻;²⁴ most recently, another Co(III)–peroxynitrite complex has been confirmed and well-characterized by IR spectroscopy, isotope labeling experiments, and density functional theory calculations.²⁵ Thus, the isolation of Cr(III)–nitrate complex **3** supports the intermediacy of a Cr(III)–peroxynitrite species. Even stronger evidence is provided by the observation that the addition of 2,4-di-*tert*-butylphenol to a solution of **2** (for which no reaction is observed) prior to NO addition leads to a 93%

yield of 2,4-di-*tert*-butyl-6-nitrophenol, indicating that the added phenol can trap the peroxynitrite intermediate.

Supplemental experiments were performed with a Cr(II)–nitrosyl complex, [Cr^{II}(12-TMC)(NO)(Cl)]Cl (**4-Cl**)²⁶ to complete a systematic study of [Cr(12-TMC)]²⁺ complexes with O₂ and NO. Reactions of metal–nitrosyl complexes with O₂ have a considerable history, including with iron,¹⁴ cobalt,¹⁵ and copper¹⁶ systems, and lead to nitrate or nitrite products through suggested peroxynitrite complex generation. Interestingly, different from the iron,¹⁴ cobalt,¹⁵ and copper¹⁶ complexes, chromium complex **4** showed no reactivity toward O₂ in acetonitrile at room temperature (Scheme 3).

Scheme 3



In summary, we have successfully constructed a systematic study of [Cr^{II}(12-TMC)]²⁺ complexes with O₂ and NO. The reactions performed are summarized in Scheme 3. **1** reacts with O₂ and NO to produce the Cr(IV)–peroxo complex **2** (reaction I) and the Cr(II)–nitrosyl complex **4** (reaction II), respectively. Complex **2** was isolated and characterized as a side-on Cr(IV)–peroxo complex. It is notable that **2** is the first TMC-ligated metal–peroxo complex to be formed from the reaction of O₂ with a reduced metal ion rather than via the use of hydrogen peroxide as the origin of the final peroxide fragment.⁵ **2** reacts with NO to give the Cr(III)–nitrate complex **3** (reaction III), which is most likely formed through a Cr(III)–peroxynitrite intermediate by means of atypical metal ion reduction chemistry. Different from many other metal–nitrosyl complexes,^{14–16} **4** did not react with O₂ (reaction IV). We are continuing our work on the systematic characterization of TMC-chelated redox-active transition-metal complexes and their O₂ and/or peroxide and/or O₂/NO-derived chemistry, which, as further seen here, is strongly influenced by the TMC ring size.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section; crystallographic data (CIF); crystal structure of **1**; UV-vis, ESI-MS, and IR spectra of **4-Cl**; and EPR spectra of **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (9) Abbreviations used: 12-TMC, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane; 14-TMC, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.
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- (18) In terms of the nature of 2'-Cl₂ in solution, the ESI-MS data for the crystals were found to be identical to those for **2** generated in situ in the reaction of **1** and O₂. This result suggests that the chloride anion instead of the aqua ligand coordinates to the Cr center in solution. Support for this supposition was provided by an experiment in which 2.2 equiv of Ag(CF₃SO₃) was added to a solution of **2**. ESI-MS analysis revealed the dominant ion present to be [Cr^{IV}(12-TMC)(O₂)(Cl)]⁺, indicating that one chloride remained bound to the chromium ion and that Ag⁺ removed only the Cl⁻ counteranion. The aqua ligand undoubtedly originates from residual solvent water and coordinates to the Cr center only in the crystal structure, probably as a result of preferred crystal packing.
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- (21) In the crystal, another nitrate anion was found as a counteranion instead of chloride; the formula of the crystal was given as [Cr(12-TMC)(NO₃)(Cl)]NO₃. See the crystallographic data and Table S1 in the SI.
- (22) The crystal of [Cr(12-TMC)(NO₃)(Cl)]NO₃ was used as an authentic sample for the calculation of the reaction yield ($\epsilon = 180 \text{ M}^{-1} \text{ cm}^{-1}$ at 415 nm).
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- (26) 4-Cl was synthesized by reacting **1** with NO(g) and characterized by UV-vis, EPR, and IR spectroscopy, ESI-MS, and elemental analysis (see the Experimental Section and Figures S4-S6 in the SI).