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Characterization of a heterobimetallic nonheme Fe(III)–O–Cr(III) species formed by O₂ activation†

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We report the generation and spectroscopic characterization of a heterobimetallic [(TMC)Fe^{III}–O–Cr^{III}(OTf)₄] species (1**) by bubbling O₂ into a mixture of Fe(TMC)(OTf)₂ and Cr(OTf)₂ in NCCH₃. Complex **1** also formed quantitatively by adding Cr(OTf)₂ to [Fe^{IV}(O)(TMC)(NCCH₃)]²⁺. The proposed O₂ activation mechanism involves the trapping of a Cr–O₂ adduct by Fe(TMC)(OTf)₂.**

Oxygen activation is generally carried out by metalloenzymes with mononuclear or homodinuclear iron or copper active sites.^{1–3} However there are two notable exceptions to this generalization, namely the heme/copper center of cytochrome oxidase essential for mammalian respiration^{4,5} and the nonheme Fe–O–Mn center of Class 1c ribonucleotide reductases found in pathogenic bacteria.^{6,7} There has been significant progress in obtaining synthetic models for the heme/copper center of cytochrome oxidase,^{8–10} but less effort has been devoted to the synthesis of nonheme (μ-oxo)heterobimetallic complexes. In 1992 Wiegardt described a series of carboxylate-bridged (TACN)Fe^{III}–O–M(Me₃TACN) (M = Cr^{III} or Mn^{III}, TACN = 1,4,7-triazacyclononane, Me₃TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane) complexes obtained by hydrolysis between FeCl₃(TACN) and MCl₃(Me₃TACN) precursors.¹¹ More recently, Fukuzumi and Nam reported the crystal structure of a novel Fe^{III}–O–Sc^{III} complex, which was obtained from the reaction of [Fe^{IV}(O)(TMC)(NCCH₃)]²⁺ (TMC = 1,4,8,11-tetramethylcyclam) with Sc(OTf)₃.¹² However, no synthetic nonheme Fe–O–M complex (where M is a non-iron metal) has thus far been generated by O₂ activation. Here we report the characterization of [(TMC)Fe^{III}–O–Cr^{III}(OTf)₄] (**1**) formed by oxygenating a mixture of Fe(TMC)(OTf)₂ and Cr(OTf)₂ in CH₃CN at –40 °C or reacting [Fe^{IV}(O)(TMC)(NCCH₃)]²⁺ with 1 eq. of Cr(OTf)₂.

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Bubbling O₂ into a solution of 1 mM Fe(TMC)(OTf)₂ and 1 mM Cr(OTf)₂ in CH₃CN at –40 °C rapidly elicited a UV-vis spectrum with bands at 358, 398, 447 and 558 nm (Fig. 1), suggesting the formation of a new species designated as **1**. This spectral pattern was not observed in the absence of either Fe(TMC)(OTf)₂ or Cr(OTf)₂ from the reaction mixture; Fe(TMC)(OTf)₂ simply did not react with O₂, but the reaction of Cr(OTf)₂ with O₂ gave rise to features at 358 and 445 nm (Fig. 1), distinct from those of **1**. Species **1** had a half-life of 10 h at –40 °C and rapidly decayed upon warming to RT. Taken together, these observations implicate both Fe and Cr in the formation of **1**.

ESI-MS analysis of the solution of **1** at –40 °C revealed dominant peaks at *m/z* 461.2 (positive mode) and 514.8 (negative mode) (Fig. S1, ESI†), which were not observed in oxygenated solutions lacking either Fe(TMC)(OTf)₂ or Cr(OTf)₂. The ions observed have masses and isotope distribution patterns that correspond to [Fe(TMC)(OTf)]⁺ and [CrO(OTf)₃][–], respectively. Furthermore, the [CrO(OTf)₃][–] peak was upshifted by 2 units when ¹⁸O₂ was used, showing the incorporation of an oxygen atom from O₂ (Fig. S2, ESI†). Based on these results, we tentatively assign **1** as a heterobimetallic [(TMC)Fe^{III}–O–Cr^{III}(OTf)₄] complex, which undergoes homolysis of the Fe–O bond to give rise to the observed mass spectral features.

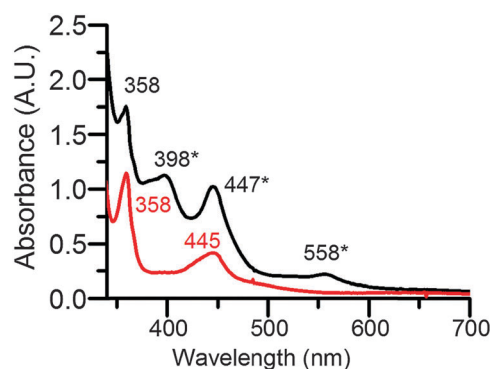


Fig. 1 UV-vis spectra observed in CH₃CN at –40 °C upon O₂ exposure of 1 mM Cr(OTf)₂ (red) and a mixture of 1 mM Fe(TMC)(OTf)₂ and 1 mM Cr(OTf)₂ (black). Bands with asterisks are associated with **1**.



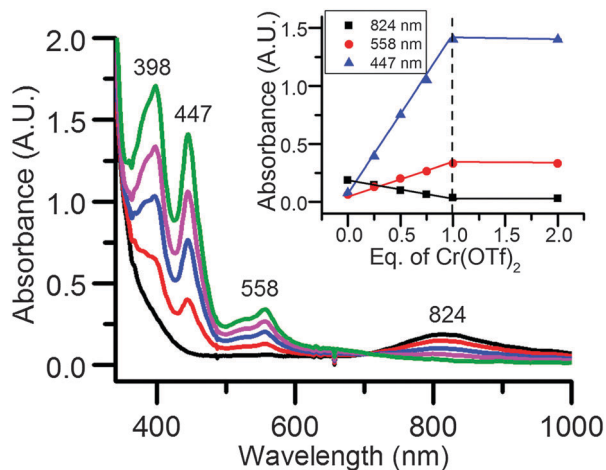


Fig. 2 UV-vis spectral titration of 0.45 mM $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{NCCH}_3)]^{2+}$ in CH_3CN at -40°C with $\text{Cr}(\text{OTf})_2$. Black, 0 eq.; red, 0.25 eq.; blue: 0.5 eq.; magenta, 0.75 eq.; green, 1 eq. Inset: Titration plot. Inset: Formation of **1** vs. eq. $\text{Cr}(\text{OTf})_2$ added into 0.45 mM $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{NCCH}_3)]^{2+}$ in CH_3CN at -40°C .

To test this hypothesis, we investigated the reaction of $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{NCCH}_3)]^{2+}$ with $\text{Cr}(\text{OTf})_2$ in CH_3CN at -40°C as a more direct means of synthesizing putative species **1**. As shown in Fig. 2, the addition of $\text{Cr}(\text{OTf})_2$ to $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{NCCH}_3)]^{2+}$ in CH_3CN solution caused the instantaneous disappearance of its characteristic 824 nm peak concomitant with the growth of bands at 398, 447, and 558 nm that are assigned to **1**. Titration experiments (Fig. 2, inset) revealed that the transformation was complete upon addition of 1 eq. $\text{Cr}(\text{OTf})_2$, strongly suggesting a 1:1 Fe:Cr stoichiometry for **1**. This solution also gave rise to ESI-MS spectra with the same dominant peaks as the complex generated by O_2 activation. A control experiment between $\text{Cr}(\text{OTf})_2$ and PhIO did not elicit the same peaks as found in **1** (Fig. S3, ESI[†]), suggesting that $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{NCCH}_3)]^{2+}$ acts more than just an oxygen atom donor to $\text{Cr}(\text{OTf})_2$. These results demonstrate that **1** can be generated by either O_2 activation or inner-sphere electron transfer.

In order to obtain structural insight, Fe K-edge X-ray absorption spectroscopy studies were carried out on **1**. As shown in Fig. S4 (ESI[†]), the Fe K-edge of **1** was found at 7124.0 eV, which is comparable to those of known $\text{Fe}^{\text{III}}(\text{TMC})$ and related complexes.¹⁴ Species **1** also exhibits a pre-edge feature that is associated with 1s-to-3d transitions with an area of 11 units. The Fourier-transformed EXAFS region revealed two prominent features at $R + \Delta \sim 1.8 \text{ \AA}$ and 3.2 \AA (Fig. 3, left). The best fit of the data (fit #8 in Table S1, ESI[†]) consisted of 1 O/N scatterer at 1.81 \AA , 5 O/N scatterers at 2.17 \AA , 4 C scatterers at 2.91 \AA and a Cr scatterer at a distance of 3.65 \AA . The 2.17 \AA and 2.92 \AA scatterers arise from the supporting TMC ligand, while the 1.81 \AA scatterer has an Fe–O distance typically found for oxo bridges in $\text{Fe}^{\text{III}}\text{--O--M}^{\text{III}}$ complexes.¹⁵ The 3.2 \AA feature corresponds to a Cr scatterer at 3.65 \AA ; its intensity derives from multiple scattering pathways due to a linear Fe–O–Cr core. Indeed, the Fe···Cr distance is typical of the metal–metal distances found for linear $\text{Fe}^{\text{III}}\text{--O--M}^{\text{III}}$ complexes^{12,16,17} and exemplified by $[(\text{py})(\text{TPP})\text{Cr}^{\text{III}}\text{--O--Fe}^{\text{III}}(\text{TMP})]$ ($r(\text{Fe} \cdots \text{Cr}) = 3.60 \text{ \AA}$; py = pyridine; TPP = tetraphenylporphyrin

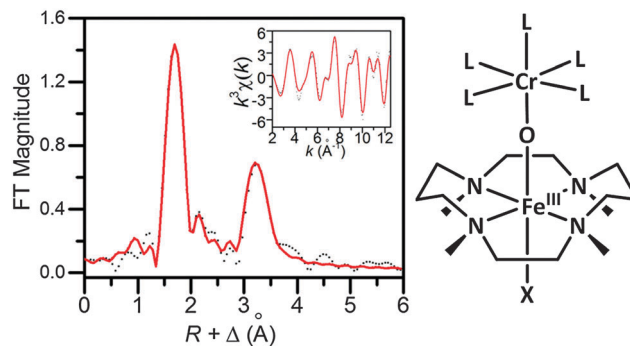


Fig. 3 Left: Fourier-transformed Fe K-edge EXAFS data for **1** (dotted black line) and corresponding best fit (solid red line, fit #8 in Table S1, ESI[†]). Inset shows unfiltered k -space data and its fit. Right: Proposed structure for **1** ($L = \text{CH}_3\text{CN}$ or OTf ; $X = \text{CH}_3\text{CN}$, NCO or NCS).

dianion; TMP = tetramesitylporphyrin dianion).¹⁸ We thus propose that **1** has the structure shown in Fig. 3 right.

The proposed structure for **1** resembles that found in the crystal structures of the recently described $[(\text{TMC})\text{Fe}^{\text{III}}\text{--O--Sc}^{\text{III}}(\text{OTf})_4(\text{L})]$ complex (**2**, $L = \text{H}_2\text{O}$ or NCCH_3).¹² However, they differ in several respects. Although the Fe···M distances are essentially identical for **1** and **2**, the respective Fe–O and M–O distances are distinct. The Fe–O distance of 1.81 \AA for **1** is 0.07 \AA longer than that found for **2**, while the Cr–O distance of 1.84 \AA (deduced from the difference between the Fe···Cr and the Fe–O distances from the EXAFS analysis, assuming $\angle \text{Fe--O--Cr} \sim 180^\circ$) is 0.07 \AA shorter than the Sc–O distance of 1.91 \AA observed for **2** in its crystal structures. The distinct M–O distances in **1** and **2** presumably reflect the difference between the more covalent Cr–O bond and the more ionic Sc–O bond, which also affect the corresponding Fe–O bond. Another feature distinguishing **1** from **2** is the intensity of the XAS pre-edge feature. Complex **1** exhibits a pre-edge area of 11 units, typical of a six-coordinate iron(III) center,^{19,20} while **2** ($L = \text{NCCH}_3$) has a much larger pre-edge area of 32 units,¹² reflecting the square pyramidal geometry of its iron(III) center. Lastly, the four methyl groups of the TMC ligand are shown in Fig. 3 right as being oriented *anti* with respect to the oxo bridge, opposite to the orientation found crystallographically for the methyl groups in **2**.¹² Although we do not have direct proof, our main argument to favor the *anti* orientation over the *syn* one is the observed immediate formation of **1** upon $\text{Cr}(\text{OTf})_2$ addition to a solution of $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{NCCH}_3)]^{2+}$. As the TMC methyl groups are oriented *anti* to the oxo moiety in the precursor,¹³ it seems unlikely that a change in their relative orientations could occur at -40°C within this very short time scale.

The likelihood of a sixth ligand for the iron(III) center in **1** is supported by the change in the spectral features of **1** upon addition of NCS^- or NCO^- . As shown in Fig. 4, there are small shifts of the three bands, as well as increases in intensity. Titration experiments showed that only 1 eq. of NCS^- or NCO^- was needed to transform **1** fully into **1-NCS** or **1-NCO** (Fig. S5 and S6, ESI[†]). ESI-MS analysis of **1-NCS** and **1-NCO** revealed respective positive mode peaks at m/z 370 and 354, corresponding to $[\text{Fe}(\text{TMC})(\text{NCS})]^+$ and $[\text{Fe}(\text{TMC})(\text{NCO})]^+$ fragment ions (Fig. S7 and S8, ESI[†]), suggesting the occupation of the axial position *trans* to the



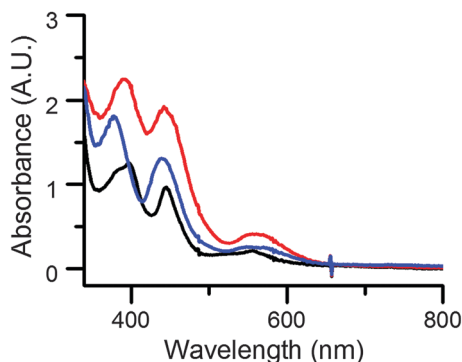


Fig. 4 UV-vis spectra of 0.3 mM **1** (black), **1-NCO** (blue), **1-NCS** (red) in CH₃CN at -40 °C. λ_{max} (ϵ_{M}) for **1**: 398 (3800), 447 (3000), and 558 (700). λ_{max} (ϵ_{M}) for **1-NCO**: 380 (6000), 438 (4200), and 560 (850). λ_{max} (ϵ_{M}) for **1-NCS**: 390 (7500), 442 (6300), and 560 (1400).

oxo bridge by these anions. Furthermore, **1-NCS** exhibits an Fe K-edge energy of 7124.3 eV, comparable to the 7124.0 eV value found for **1**. **1-NCS** also exhibits a pre-edge feature with an area of 9 units (Fig. S9, ESI[†]), which is close to the 11 units found for **1** but much smaller than the 32 units associated with **2**, showing that a six-coordinate iron(III) center in **1-NCS** is maintained. EXAFS analysis of **1-NCS** shows the presence of a linear Fe–O–Cr core like that in **1**, but with a 1.85 Å Fe–O bond and an Fe...Cr distance of 3.67 Å (Table S2 and Fig. S10, ESI[†]). The observed lengthening of the Fe–O bond can be rationalized by the axial NCS[−] binding to the iron(III) center. Based on all the information above, **1** is proposed to be a heterobimetallic μ -oxo species with an Fe–O–Cr core, and the Fe atom has a 6-coordinate environment with the axial position available for ligand substitution (Fig. 3, right).

Complex **1** was further studied by EPR and resonance Raman spectroscopy. It is EPR-silent, which is as expected due to antiferromagnetic coupling mediated by the oxo bridge between the Fe(III) and the Cr(III) centers, as seen for two other Fe(III)–O–Cr(III) complexes.^{11,18} Excitation of **1** with a 568.2 nm laser elicits a resonance-enhanced vibration at 773 cm^{−1} (Fig. 5), which falls within the 700–900 cm^{−1} range found for the ν_{as} (Fe–O–Fe) modes of oxo-bridged diiron(III) complexes.²¹ This assignment is corroborated by the observed downshift of

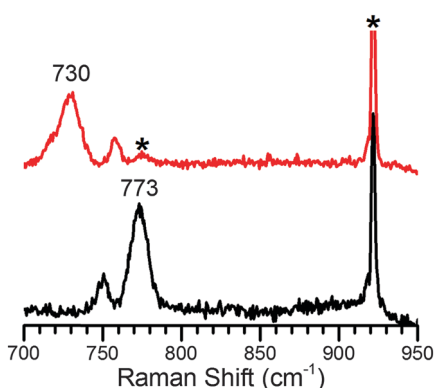
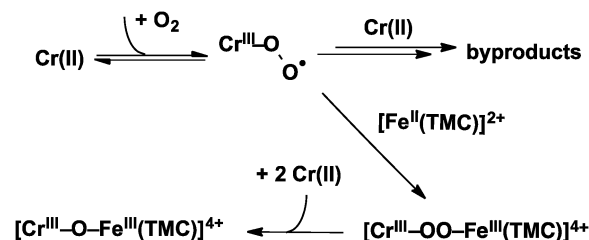


Fig. 5 Resonance Raman spectra of **1** in CH₃CN (λ_{ex} = 568.2 nm, 20 mW, 77 K). Black, ¹⁶O; red, ¹⁸O. Asterisks denote solvent peaks.

this vibration to 730 cm^{−1} upon ¹⁸O-substitution into the oxo bridge. Although a 35 cm^{−1} downshift for a diatomic Fe–O mode is predicted by Hooke's Law, the experimentally obtained ¹⁸O shift is 43 cm^{−1}. This larger than predicted shift has also been reported for corresponding vibrations of several oxo-bridged diiron(III) complexes.²¹ There is also a weaker feature found at 746 cm^{−1} that exhibits an upshift of 7 cm^{−1} upon ¹⁸O-substitution; this is an unusual observation that we cannot explain. The 773 cm^{−1} vibration is also weakly enhanced upon 514.5 nm excitation but not observed with 457.9 or 647.1 nm irradiation, suggesting that the 558 nm absorption band can be associated with a transition of the Fe–O–Cr moiety.

With the nature of **1** reasonably well characterized, we return to an analysis of the O₂ activation reaction results. Based on the molar extinction coefficients of **1** determined from the stoichiometric conversion of [Fe^{IV}(O)(TMC)(NCCH₃)₂]²⁺ to **1** by Cr(OTf)₂, we conclude that **1** is produced in about 30% yield from the reaction of equimolar amounts of Fe(TMC)(OTf)₂ and Cr(OTf)₂ to O₂. The yield of **1** was unchanged by increasing the Fe(TMC)(OTf)₂/Cr(OTf)₂ ratio from 1 to 10 ([Cr(OTf)₂] = 1 mM) (Fig. S11, ESI[†]), suggesting that Cr(OTf)₂ is the limiting reagent. In contrast, the yield of **1** increased to 95% when the concentration of Fe(TMC)(OTf)₂ was fixed at 1 mM and the Cr(OTf)₂ concentration was raised from 1 mM to 10 mM (Fig. S12, ESI[†]). Therefore, the % yield of **1** is dependent on the amount of Cr(OTf)₂, but not on the amount of Fe(TMC)(OTf)₂. These results can be rationalized by the O₂ activation pathway proposed in Scheme 1, in which the four electrons needed to reduce O₂ to the oxidation level of water are provided by 1 eq. Fe(TMC)(OTf)₂ and 3 eq. Cr(OTf)₂, not unlike the four redox-active centers required for O₂ activation by cytochrome oxidase.⁴ In the present case, we postulate that O₂ initially binds to the O₂-sensitive Cr(OTf)₂ to form a transient adduct (analogous to that characterized by Nam in the reaction of [Cr^{II}(TMC)Cl]⁺ with O₂²²) that is then trapped by Fe(TMC)(OTf)₂ to generate a yet unobserved Fe^{III}–O–O–Cr^{III} peroxo-bridged intermediate. This intermediate is then reduced by another 2 eq. Cr(OTf)₂ to form **1**. Thus the ca. 30% yield of **1** observed under limiting Cr conditions reflects the 1:3 stoichiometry of Fe(TMC)(OTf)₂/Cr(OTf)₂ needed to make **1**. On the other hand, under limiting Fe conditions, enough Cr–O₂ adduct is formed to react with all the available Fe(TMC)(OTf)₂ to convert the latter almost quantitatively to **1**.

In conclusion, a heterobimetallic nonheme species **1** with an Fe–O–Cr core has been generated from both O₂ activation and



Scheme 1 Proposed mechanism for formation of **1** by O₂ activation.



inner-sphere electron transfer. The structure of **1** was deduced by a combination of UV-vis, resonance Raman, and X-ray absorption spectroscopic methods and ESI-MS. The O₂ activation mechanism for the formation of **1** is proposed to be analogous to that of cytochrome oxidase, where the initially formed O₂ adduct is reduced by the other three redox-active metal centers in the enzyme, demonstrating a general strategy for O₂ activation. Furthermore, **1** represents only the second example of a hetero-bimetallic M–O–Fe(TMC) complex, which can shed light on the effects of Lewis acidic metal centers on the redox properties of high-valent M = O species.²³ Such interactions are considered important for facilitating the oxidation of water by the CaMn₄O₅ cluster of the oxygen evolving complex in photosynthesis.^{24–26} Along these lines, Lloret-Fillol and coworkers have demonstrated the formation of a related Fe^{IV}–O–Ce^{IV} intermediate in the oxidation of water by a nonheme iron catalyst with Ce(NH₄)₃(NO₃)₆ as oxidant.²⁷

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