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Identification of an “End-on” Nickel−Superoxo Adduct, $[Ni(tmc)(O_2)]^+$

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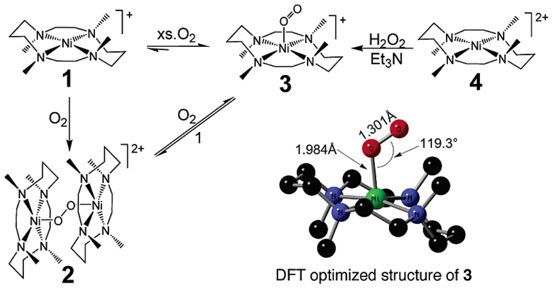
Transition metal dioxygen adducts have attracted the attention of chemists for decades. Inspiration for such studies derives from the importance of these species in aerobic respiration, biocatalysis, and synthetic oxidations.[1,2] The structures of several dioxygen adducts have been elucidated, and in numerous cases, structure−reactivity correlation paradigms have emerged.[3] Recent advances in the area of $Ni-O_x$ complexes[4,5] have benefited from the accessibility of isolable Ni^+ precursors, sufficiently electron-rich to reduce dioxygen as demonstrated through spectroscopic studies of the resulting products. Specifically, efforts from these laboratories have led to the elucidation of $Ni(\eta^2\text{-}O_2)$,[6] $Ni_2(\mu\text{-}1,2\text{-}O_2)$,[7,8] and $Ni_2(\mu\text{-}O)_2$ motifs.[9] The identity of the supporting ligand is critical both for the success in preparing the Ni^+ complexes and for directing the reactions toward variable product structures. This work finds some inspiration in the early reports of Kimura and co-workers that a Ni^{3+}−superoxo species hydroxylates aromatic substrates, thus exhibiting monooxygenase activity.[10] Subsequent efforts by others established a seminal role for the ligand in autooxidation.[11] Here, we report the preparation, spectroscopic characterization, and reactivity of a Ni^{2+}−superoxo complex.

Recently, we have shown that the low temperature addition of O_2 to [Ni(tmc)](OTf) (**1**) (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; OTf = CF_3SO_3) yields a transient bridging peroxo dimer, $\{[Ni(tmc)]_2(\mu\text{-}O_2)\}(OTf)_2$ (**2**), possibly via the formation of a 1:1 $Ni-O_2$ intermediate.[7] Indeed, $[Ni(tmc)(O_2)](OTf)$ (**3**) is accessible when the oxygenation reaction is performed such that O_2 is in excess even after the initial formation of **2** (Scheme 1). In a typical experiment, dry, high-purity O_2 is bubbled into a stirring THF solution of **1** at − 78 °C for 5 min. The reaction progression is monitored by UV−vis spectral changes. Formation of **3** under these conditions appears clean as evidenced by the observation of isosbestic points for the conversion of **2** to **3** (SI, Figure S1). Alternatively, **3** can be generated in modest yield by the addition of 10 equiv of H_2O_2 to a reaction solution containing $[Ni(tmc)](X)_2$ (**4** , where X = OTf^-, ClO_4^-) and NEt_3 (10 equiv) in either CH_3CN or CH_3OH at 25 °C (SI, Figure S2).[12]

Scheme 1



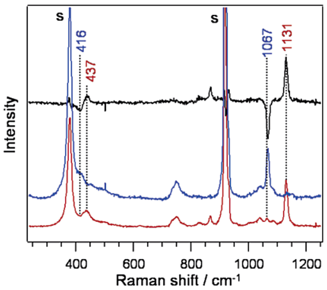


Figure 1. Resonance Raman spectra of **3** in CH_3CN obtained upon excitation at 407 nm at −20 °C. Red/blue traces: samples prepared from **4** with $H_2{}^{16}O_2/H_2{}^{18}O_2$; black trace: difference spectrum, $({}^{16}O-{}^{18}O)$. The peaks marked with “s” are ascribed to the solvent.

The optical spectrum of **3** is dominated by a UV absorption band with a λ_{max} of 345 nm in THF ($\epsilon = 1500\ M^{-1}\ cm^{-1}$, shoulder at 328 nm). Resonance Raman spectra obtained upon excitation at 407 nm exhibit two vibrational features that are oxygen isotope sensitive (Figure 1 ; Figures S3 and S4). Specifically, the bands at 1131 and 437 cm^{-1} downshift to 1067 and 416 cm^{-1}, respectively, in samples of **3** prepared from ^{18}O-labeled sources (either $H_2{}^{18}O_2$ or $^{18}O_2$). The more intense, higher-energy feature is assigned to the $\nu(O-O)$ mode based on its frequency and the magnitude of the isotopic shift ($\nu({}^{16}O-{}^{16}O)/\nu({}^{18}O-{}^{18}O) = 1.060$; calcd 1.061 for a harmonic oscillator). The lower-frequency mode is ascribed to the $\nu(Ni-O)$ vibration ($\nu(Ni-{}^{16}O)/\nu(Ni-{}^{18}O) = 1.050$; calcd 1.048). The frequency of the $\nu(O-O)$ mode provides an excellent probe of the extent of charge transfer from Ni^+ to the dioxygen ligand, with the Ni^{2+}−superoxo and Ni^{3+}−peroxo resonance structures representing the two limiting descriptions.[13] For **3**, the high value of 1131 cm^{-1} is in accord with a Ni^{2+}−superoxo description.[5,14,15] Electrospray mass spectrometry (ESI MS) analysis of CH_3CN solutions of **3** supports its formulation as a monomer bearing an O_2 unit (Figure S5).

X-ray absorption spectroscopy (XAS) was performed to probe the coordination sphere and oxidation state of nickel. In the near-edge region, a weak, electric-dipole forbidden Ni 1s → 3d transition is observed at 8333.9 keV, consistent with the +2 oxidation state when compared to a related complex [Ni(tmc)(OH)](OTf) (Figure S6). Best-fit models of the extended X-ray absorption fine structure (EXAFS) data of **3** include an O/N scatterer at 1.98 Å and four

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N/O scatterers at 2.17 Å, consistent with "end-on" superoxide coordination (SI for details).

Complex **3** is EPR active (Figures S8 and S9), displaying a rhombic signal with *g* values of 2.29, 2.21, and 2.09. Samples of **3** prepared from $^{17}O_2$ show minor EPR line broadening (estimated at ~10 G), indicating that very little unpaired spin density resides on the O_2 ligand.[6] These observations suggest a spin coupled $S = {}^{1}/_{2}$ ground state[16] in agreement with literature precedents of transition metal superoxo species.[1]

To further establish the geometric and electronic structures of **3**, density functional theory (DFT) computational studies were performed on several models, considering both side-on and end-on geometries as well as high-spin (HS, $S = {}^{3}/_{2}$) and low-spin (LS, $S = {}^{1}/_{2}$) ground states (SI for details). For both spin systems, the geometries converged to end-on structures (Scheme 1, inset), clearly indicative that the end-on geometry is heavily favored over a side-on structure.

Complex **3** oxidizes PPh_3 to $OPPh_3$ in quantitative yield, and the reaction exhibits a first-order dependence on PPh_3 (Figures S10 and S11). Samples of **3** prepared from $H_2{}^{18}O_2$ produce $^{18}OPPh_3$ (Figure S12), establishing the source of the oxygen incorporated into the product. $[PhTt^{Ad}]Ni(\eta^2\text{-}O_2)$ displays analogous electrophilic propensity for PPh_3, suggesting that side-on and end-on $[NiO_2]^+$ moieties engender similar reactivity characteristics.[6] However, the complex **3** does not react with less reactive substrates such as sulfides and olefins.

Facile generation of complex **3** by the addition of oxygen to the peroxo-bridged dimer **2** provides for an interesting kinetics scenario. The most straightforward interpretation is that addition of oxygen to both **1** and **2** is rate limiting, signifying that **1** reacts with **3** faster than it reacts with dioxygen. Ongoing experiments are aimed at establishing the full kinetic profiles of the formation and decay of **2** and **3**, along with DFT analysis of the thermodynamics of the respective pathways.[17]

The mechanism by which **3** is formed from the Ni^{2+} species **4** and excess H_2O_2 is of interest as it represents a valuable synthetic route to $M(O_2)$ adducts. Shiren et al. reported the preparation of a binuclear superoxo adduct, $Ni_2(\mu\text{-}O_2)_2$, via the reaction of $Ni_2(\mu\text{-}O)_2$ with excess H_2O_2.[5] The analogous pathway seems unlikely in the present case as the tmc macrocycle is constrained from folding into a conformation necessary for $Ni_2(\mu\text{-}O)_2$ formation.[18] Formation of a Ni^{2+}-OOH intermediate which quickly dimerizes in the presence of base to yield **2** seems unlikely as **2** has not been observed via this route. Therefore, an intriguing alternative mechanism invokes the intermediacy of a high-valent oxonickel moiety that reacts with H_2O_2 directly. This process would be akin to the second step of the catalase mechanism in which an oxoiron porphyrin (compound I) oxidizes H_2O_2 to O_2.[19] In the present case, the O_2 would be available to react with $[Ni(tmc)]^+$ to generate **3**. More detailed investigations are needed to understand the mechanism of the formation of **3** in the reaction of **4** and H_2O_2 in the presence of base.

Significantly, **3** represents the first example of an end-on dioxygen complex in nickel coordination chemistry; side-on superoxo[6] and peroxo[20] adducts have been described previously. These diverse Ni/O_2 adducts provide the opportunity to evaluate inherent reactivity differences between the two coordination modes, which is a subject of considerable current interest.[21]

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Note Added after ASAP Publication. In the version published on the Internet October 14, 2006, the page number for ref 8 was incorrect. In the version published on the Internet October 19 and in the print version the page number is correct.

Supporting Information Available: Experimental details, characterization data, and computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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