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A Monomeric Nickel–Dioxygen Adduct Derived from a Nickel(I) Complex and O_2

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The nickel(I) complex [PhTt^{Ad}]Ni(CO) (PhTt^{Ad}, phenyltris((1-adamantylthio)methyl)borate) reacts with O_2 generating a 1:1 species identified as a side-on dioxygen adduct based on its spectroscopic properties as supported by DFT computational results and by its reactivity. The Ni EXAFS data are fit to a S_3O_2 coordination environment with short Ni–O distances, 1.85 Å. The brown complex displays a rhombic EPR signal with *g* values of 2.24, 2.19, 2.01. DFT and INDO/S-CI computations replicate the EXAFS and EPR features and suggest that **2** is a side-on $[NiO_2]^+$ complex with geometric and electronic properties that are best rationalized in terms of a highly covalent Ni(II)–superoxo description. [PhTt^{Ad}]Ni(O_2) oxidizes PPh_3 to $OPPh_3$, NO to NO_3^-, and [PhTt^{tBu}]Ni(CO) to the nonsymmetric [PhTt^{Ad}]Ni(μ-O)$_2$Ni[PhTt^{tBu}] dimer.

Nickel−dioxygen intermediates have been invoked in a number of stoichiometric and catalytic reactions. For example, nickel(II) azamacrocycles activate O_2 yielding products resulting from aromatic[1] and aliphatic[2] (ligand-based) C−H activation. Burrows has deployed related complexes as oxidative probes of the structure of proteins and DNA, albeit with more reactive oxidants, i.e., H_2O_2 and $KHSO_5$.[3] While metal-bound reduced dioxygen species have been suggested as the active reagents for these transformations, thorough characterization of the corresponding intermediates is generally lacking.[4] Recently, we reported that the Ni(I) complex [PhTt^{tBu}]Ni(CO) forms the purple dimer [(PhTt^{tBu})Ni]$_2$(μ-O)$_2$, upon low-temperature exposure to O_2.[5,6] Analogous bis-μ-oxo Ni_2O_2 cores are accessible from Ni(II) precursors using H_2O_2 as the oxidant.[7] To explore the mechanism by which the bis-μ-oxo dimer is generated from O_2 and to prepare intermediates that are more reactive toward exogenous substrates, we sought to redesign the [PhTt^{tBu}] ligand so as to access a Ni(I) complex that would sterically preclude bis-μ-oxo dimer formation.[8] Herein, we report on the successful pursuit of this strategy which led to the discovery of a side-on dioxygen complex of nickel, shown to be an intermediate to bis-μ-oxo dimer formation.

Exposure of toluene or THF solutions of [PhTt^{Ad}]Ni(CO), **1**,[8] to dioxygen produced a thermally sensitive, brown intermediate [PhTt^{Ad}]Ni(O_2), **2**, that formed with $k_{obs} = 8.4(6) \times 10^{-3}$ s^{-1} (toluene, −70 °C), Scheme 1. The composition of **2** was deduced by its unique spectroscopic features[9] and supported by its reactivity. The optical spectrum of **2** in THF exhibits bands at λ_{max} (ϵ [M^{-1} cm^{-1}]) 310 (5900), 386 (2900), 450 (2500), and 845 (350) nm. In the UV region the spectrum is strikingly similar to those of Co[10] and Cu[11,12] side-on dioxygen complexes. In contrast, [(PhTt^{tBu})Ni]$_2$(μ-O)$_2$ dis-

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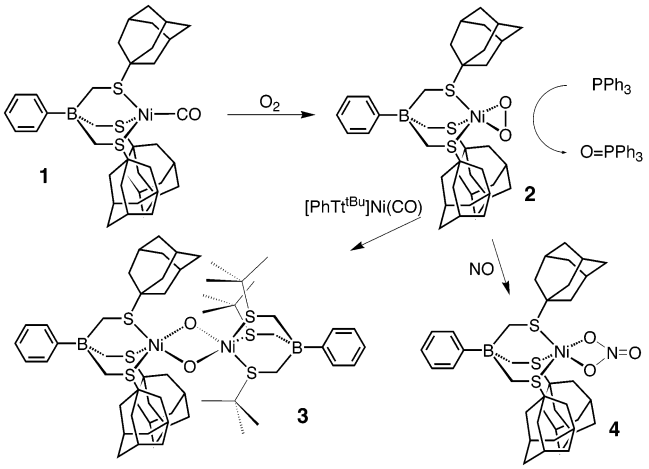
Scheme 1



plays intense features at 410 nm (ϵ = 6000 M^{-1} cm^{-1} per Ni) and 565 nm (8000), the latter ascribed to a O→Ni charge transfer (CT) transition.[6] The electrospray ionization mass spectrum of **2** reveals a positive ion cluster at *m*/*z* of 705. The isotope distribution pattern agrees with that calculated for a species of empirical formula $[PhTt^{Ad}]Ni(O)^+$. Furthermore, the signal shifts to higher mass by two units for samples of **2** derived from $^{18}O_2$. The isotope-sensitive ion signals confirm that oxygen is a constituent of the complex, although there is no indication of the parent ion in the mass spectrum.

2 displays paramagnetically shifted ^1H NMR spectral resonances and an $S = {}^1/_2$ EPR spectrum at 4.2 K.[9] The rhombic signal with *g* values of 2.24, 2.19, and 2.01 supports the monomeric formulation and is indicative of a $(d_{z^2})^1$ electron configuration typically observed for Ni(III) species.[13] The Ni coordination sphere has been characterized by Ni K edge X-ray absorption spectroscopy (XAS). A preedge 1s → 3d transition occurs at 8331.4 eV, a value 1 eV greater than that for the Ni(I) precursor, **1**, but 1 eV lower than observed in the Ni(III)$_2$ dimer, $[(PhTt^{tBu})Ni]_2(\mu\text{-}O)_2$, thus suggesting a Ni(II) oxidation state.[5] The Ni EXAFS data corroborate the monomeric nature of **2**, Figure 1. Specifically, there is no indication of a short M- - -M vector as observed for $[(PhTt^{tBu})Ni]_2(\mu\text{-}O)_2$ and deemed diagnostic of bis-μ-oxo rhombs.[14] The Ni ligation consists of three sulfur atoms at Ni−S_{av}, 2.26 Å, and two oxygen atoms at Ni−O_{av}, 1.85 Å. The latter value is in the range found by X-ray diffraction for M−O distances in side-on O_2 complexes.[10,12,15] Although the accuracy of coordination number assignment by EXAFS

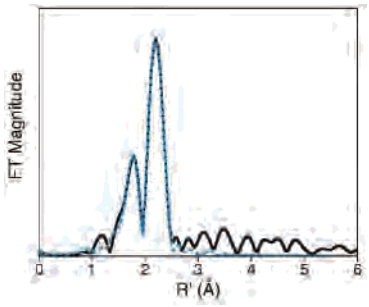


Figure 1. Fourier transform of EXAFS data (solid black line) and simulation (dashed blue line) for **2** (*k*, 2−16.5 $Å^{-1}$). Simulation: 3 S at 2.26 Å (σ^2, 0.03) and 2 O at 1.85 Å (0.03).

is limited, the data are fit much better assuming two O ligands rather than one, consistent with a side-on coordination of the dioxygen ligand. Side-on vs end-on O_2 coordination could in principle be distinguished spectroscopically via vibrational analysis of the $^{16}O^{18}O$ isotopomer.[10,11,16] However, resonance Raman spectroscopic experiments on **2** have failed to identify oxygen-isotope sensitive bands, presumably due to the low intensity of the optical features associated with the $[NiO_2]^+$ unit.

To further corroborate the structural assignment of **2**, a computational analysis of hypothetical side-on and end-on O_2 complexes (possessing a suitably truncated derivative of the $PhTt^{Ad}$ ligand)[9] was undertaken. The two models were energy minimized by DFT using the B3LYP hybrid functional,[17] and for the optimized structures the *g* values were obtained from semiempirical INDO/S-CI computations as implemented in ORCA.[9,18] These calculations yielded principal *g* values of 2.29, 2.22, and 2.09 for the side-on O_2 complex and 2.44, 2.33, and 2.21 for the end-on complex. While the former values are consistent with the EPR data, the latter are considerably too high, arguing against the presence of an end-on bound O_2 moiety in **2**. In further support of a side-on O_2 description of **2**, calculated ^{17}O hyperfine coupling constants for this model indicate very little unpaired spin density on the O_2 ligand, which concurs nicely with the observation that the EPR spectrum of **2** prepared with $^{17}O_2$ shows no resolvable coupling.[9] The side-on structure is square pyramidal, high-spin Ni(II) with two sulfurs and two oxygens in the basal plane and the remaining sulfur in the apical position (Figure 2a, left). The calculated average Ni−S and Ni−O bond distances of 2.33 and 1.87 Å, respectively, are in good agreement with those determined by EXAFS spectroscopy, while the computed O−O bond length of 1.38 Å appears characteristic of a peroxo spe-

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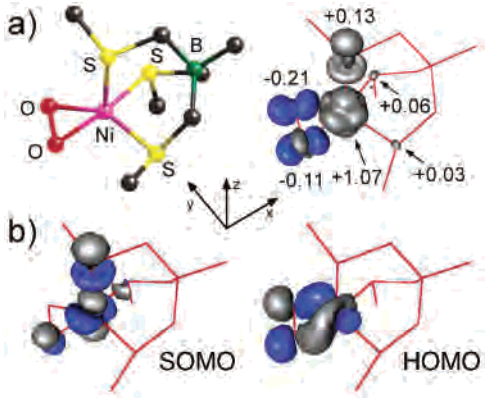

Figure 2. (a) Geometric structure (left) and total unpaired spin density distribution (right). Unpaired spin densities on individual atoms are indicated. The coordinate system is defined by the *g* matrix orientation as obtained from INDO/S-CI computations. (b) Key natural orbitals of **2** as obtained from spin-unrestricted DFT computations.

cies.[19,20] However, as DFT computations on peroxo species typically yield O−O bond lengths greater than 1.4 Å,[15b] this result actually agrees well with the XAS data, also indicating that **2** possesses substantial Ni(II)−superoxo character. Nonetheless, the DFT-computed total unpaired spin density for **2** is predominantly located on the Ni center (Figure 2a, right). These findings suggest an electronic structure in which the unpaired electron in the Ni $d_{x^2-y^2}$ orbital and the O_2^- radical are strongly antiferromagnetically coupled, consistent with the fact that the HOMO (Figure 2b) possesses nearly identical contributions from the Ni $d_{x^2-y^2}$ and the in-plane O_2^- π^* orbitals. The remaining single unpaired electron resides primarily in the Ni d_{z^2} orbital (SOMO, Figure 2b), which explains the general features of the EPR spectrum and the lack of sizable hyperfine broadening in samples of **2** prepared with $^{17}O_2$. A similar model has been invoked to explain the EPR properties of {FeNO}^{7} systems, for which detailed studies by Solomon and co-workers revealed that the observed $S = {}^3/_2$ ground state arises from strong antiferromagnetic coupling between the Fe(III) center ($S = {}^5/_2$) and NO^- ($S = 1$).[21] Together, the spectroscopic and computational results suggest that **2** is a side-on $[NiO_2]^+$ complex with geometric and electronic properties that are consistent with a formal Ni(II)−superoxo description.[19,20]

Preliminary exploration indicates the reactivity of **2** to be rich, Scheme 1. Unlike $[(PhTt^{tBu})Ni]_2(\mu\text{-}O)_2$, **2** transfers an equivalent of oxygen to PPh_3, generating $OPPh_3$ quantitatively; ^{18}O labeling confirms O_2 as the source. The electrophilic character of **2** is reminiscent of reactivity observed for a Ni(II)−peroxo adduct.[22] **2** oxidizes nitric oxide to nitrate forming $[PhTt^{Ad}]Ni(NO_3)$ (the nitrite complex, $[PhTt^{Ad}]Ni(NO_2)$ is a minor (15%) product; ^1H NMR spectral quantitation and comparison with authentic samples). More interestingly, **2** reacts with the smaller Ni(I) precursor, $[PhTt^{tBu}]Ni(CO)$, forming the corresponding purple bis-μ-oxo dimer, **3** (85% yield), with different borato ligands on each Ni.[23] Also, oxygenation of $[PhTt^{tBu}]Ni(CO)$ proceeds initially to an intermediate with optical and EPR spectral parameters similar those observed for **2**.[13] The short-lived $[PhTt^{tBu}]Ni(O_2)$ decays, yielding $[(PhTt^{tBu})Ni]_2(\mu\text{-}O)_2$. These observations indicate that **2** and the related side-on O_2 complex, $[PhTt^{tBu}]Ni(O_2)$, are bona fide intermediates in bis-μ-oxo Ni(III)$_2$ dimer formation.

In summary, spectroscopic analysis of the thermally sensitive brown intermediate, **2**, produced from dioxygen supports the structural assignment of a side-on dioxygen adduct best described as a Ni(II)−superoxo complex in which the superoxide radical is antiferromagnetically coupled to the high-spin Ni(II) center to yield an $S = {}^1/_2$ EPR spectrum characteristic of a d_{z^2} ground state electronic configuration. Electronic structure calculations provide strong support for the side-on coordination mode as the calculated EPR *g* values and metric parameters agree well with those determined experimentally.[9] The reactivity of **2** points to an O_2 adduct that is competent to transfer O_2 to NO and an O atom to PPh_3. **2** is an intermediate in bis-μ-oxo Ni(III)$_2$ dimer generation provided the sulfur substituents of its Ni(I) reaction partner are sufficiently small so as to allow for close approach of two metals.

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Supporting Information Available: Synthetic procedures along with computational and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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