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Dioxygen Activation by a Nickel Thioether Complex: Characterization of a $Ni^{III}_2(\mu\text{-}O)_2$ Core

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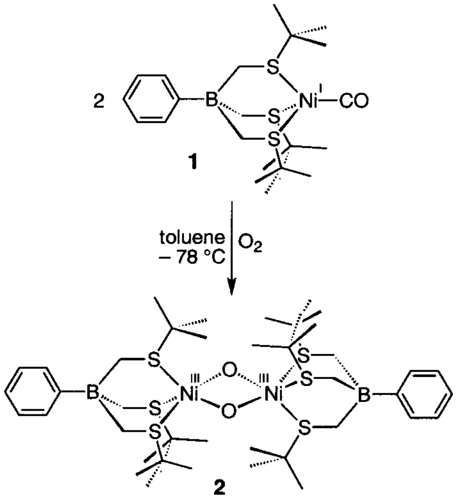
The activation of dioxygen by nickel complexes may be considered to proceed via several distinct pathways. While disulfide formation from outer sphere electron transfer is the most common result of oxygen sensitivity in nickel thiolato complexes, certain derivatives generate sulfur oxygenates with maintenance of the coordination sphere. In the thoroughly studied *cis*-diaminodithiolato complex Ni(BME-DACO),[1] Darensbourg has detailed the mechanism(s) by which the metallosulfones and metallosulfoxides are formed.[2] The thiolate sulfurs are the sites of highest nucleophilicity, an observation supported by ab initio calculations showing the sulfur p orbital as the HOMO.[3] Alternatively, inner sphere O_2 reduction transpires at the metal generating a metal-bound reduced oxygen species, i.e., superoxide, peroxide, or oxide. For example, a nickel(II) pentaazamacrocycle complex has been shown to catalyze the aerobic oxidation of benzene to phenol.[4] Ni(III)-superoxide has been inferred as the intermediate species responsible for this transformation. Related nickel azamacrocycles also activate O_2, ultimately yielding products derived from ligand C−H hydroxylation.[5] Herein we report spectroscopic characterization of a $Ni(III)_2(\mu\text{-}O)_2$ species produced by oxygenation of a nickel(I) presursor, Scheme 1. Collectively the unique spectroscopic features of the $Ni(III)_2(\mu\text{-}O)_2$ core establish the structure unambiguously. While in recent years this structural motif has been established,[6] the present report extends this class to include a nickel complex derived from O_2. Furthermore, this is the initial account of a $M_2(\mu\text{-}O)_2$ core supported by sulfur ligands.

Scheme 1



Oxygenation of $[PhTt^{tBu}]Ni(CO)$,[7] **1**, in toluene led to a dramatic color change from pale yellow to deep purple generating a thermally sensitive species formulated as $[(PhTt^{tBu})Ni]_2(\mu\text{-}O)_2$, **2**, based on its spectroscopic features. Two intense optical absorption bands are present at −60 °C, λ_{max} (ϵ, M^{-1} cm^{-1}) 410 (12 000) nm and 565 (16 000) nm that are ascribed to charge-transfer transitions, Figure 1.[8] The bands are more intense and red shifted approximately 100 nm compared to those found for the H_2O_2-derived $[(Tp^{Me3})Ni]_2(\mu\text{-}O)_2$.[9] Clearly, the nature of the supporting ligand is significant in determining the optical transitions. **2** is diamagnetic as evidenced by the ESR silence at 77 K and the appearance of its ^1H NMR spectrum. At −60 °C in toluene-d_8, all proton resonances appear between 0 and 10 ppm. Most notably, there is a single, sharp resonance for the three *tert*-butyl groups indicating equivalent magnetic environments for the thioether arms of the borato ligands in **2** under these conditions. While the expected square pyramidal geometry would give rise to distinct basal and apical thioether coordination, these positions must be equilibrating rapidly on the NMR time scale. The observed diamagnetism is consistent with an anti-ferromagnetically coupled bimetallic complex. The electrospray ionization mass spectrum of **2** reveals a prominent positive ion cluster at *m*/*z* of 471. The isotope distribution pattern is identical to that calculated for the empirical formula of the monomeric cation, $[PhTt^{tBu}]Ni(O)^+$. Furthermore, the ion cluster shifts two mass units to *m*/*z* of 473 for samples of **2** prepared with $^{18}O_2$. There was no evidence for the parent ion dimer species. The isotope-sensitive ion signals confirm dioxygen as the source of the oxo ligands.

Establishment of the $Ni(III)_2(\mu\text{-}O)_2$ core structure is provided by the resonance Raman spectra of **2**. Excitation at 600 nm yields an intense feature at 585 cm^{-1} (Figure 1, inset). This feature is not present in samples of **2** warmed to 25 °C permitting for decomposition. The resonance enhancement excitation profile of the 585 cm^{-1} vibrational mode correlates with the optical band at 565 nm.[8] Samples of **2** prepared under an $^{18}O_2$ atmosphere exhibit a Raman feature at 555 cm^{-1}. The 30 cm^{-1} shift upon $^{18}O_2$ incorporation agrees with the value calculated for a simple harmonic Ni−O oscillator, 28 cm^{-1}. The energy of this band is too low for the O−O stretching vibration of a coordinated superoxide or peroxide ligand. However, the frequency is similar to that of bands observed in $M_2(\mu\text{-}O)_2$ cores of Cu, Fe, and Mn for which the symmetric A_g $M_2(\mu\text{-}O)_2$ mode has been assigned.[10] For example, in $[(L^{TMPD}Cu)_2(\mu\text{-}O)_2]^{2+}$ the A_g band appears at 608 cm^{-1} ($^{18}O_2$: 581 cm^{-1}).[10c]

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(1) Abbreviations: BME-DACO, 1,5-bis(2-mercaptoethyl)-1,5-diazacyclooctanate; $PhTt^{tBu}$, phenyltris((*tert*-butylthio)methyl)borate; Tp^{Me3}, tris(3,4,5-trimethylpyrazolyl)hydroborate; L^{TMPD}, *N,N,N′,N′*-tetramethylpropanediamine.

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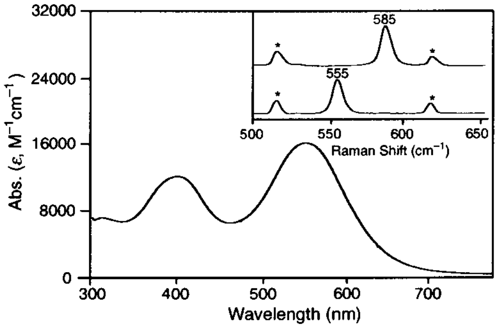

Figure 1. Visible spectrum of **2** in toluene at −60 °C. Inset: Resonance Raman spectra obtained in toluene using 600-nm excitation for samples prepared with $^{16}O_2$ (upper) and $^{18}O_2$ (lower). Solvent peaks are marked with an asterisk.

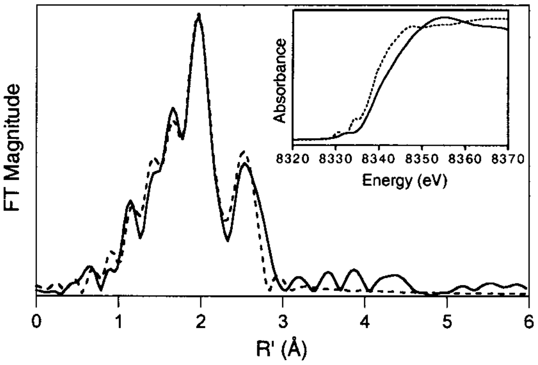

Figure 2. Fourier transform of EXAFS data (solid line) and simulation (dashed line) for **2** (k, 2−16.5 Å^{-1}). Simulation: 3 S at 2.34 Å (σ^2, 0.003), 2 O at 1.82 Å (0.002), 1 Ni at 2.83 Å (0.003). Inset: Edge region for **1** (dashed line) and **2** (solid line).

The nickel coordination sphere in **2** has been characterized by Ni K edge X-ray absorption spectroscopy (XAS). The energy of the edge absorption, 8341.3 eV, is consistent with the Ni(III) oxidation state and is 2.5 eV higher in energy than the Ni(I) precursor, **1**, Figure 2 (inset).[11] The Ni EXAFS data corroborate the $Ni(III)_2(\mu\text{-}O)_2$ core structure, Figure 2.[8] The nickel ligation consists of two oxygen scatterers at short distances, $Ni-O_{ave}$, 1.82 Å, three sulfur scatterers at $Ni-S_{ave}$ 2.34 Å, and one nickel scatterer at 2.83 Å. The short Ni- - -Ni vector identifies **2** as a dimer in accord with its observed diamagnetism. The Ni−O and Ni- - -Ni distances are similar to the corresponding metrics for $[(Tp^{Me3})Ni]_2(\mu\text{-}O)_2$ established by single-crystal X-ray analysis.[9]

Thermally sensitive **2** decomposed cleanly (isobestic point, 345 nm) at 25 °C with a half-life of ca. 5 min to a single, as yet to be determined product (λ_{max}, 320 nm {5000 M^{-1} cm^{-1}}). Related high-valent $M_2(\mu\text{-}O)_2$ complexes are susceptible to intramolecular ligand C−H oxidation and ligand N-dealkylation as primary thermal degradation pathways.[12] The C−H activation appears to proceed via a concerted mechanism in which quantum mechanical tunneling has been suggested based on large H/D kinetic isotope effects.[12] In **2** there are two ligand positions that are potential targets for oxidation. The *tert*-butyl substituents are proximate to the $Ni(III)_2(\mu\text{-}O)_2$ core and, therefore, are potentially accessible for C−H activation. Alternatively, thioether sulfurs are prone to oxidation to sulfoxides. However, preliminary FT-IR spectral analysis indicates that **2** does not yield sulfur oxygenates.

In summary, spectroscopic analysis of the thermally sensitive purple intermediate produced via reaction of the nickel(I) complex, **1**, with dioxygen establishes the structure as the bis-μ-oxo species, **2**. Oxygenation with $^{18}O_2$ confirmed the source of the oxo ligands as dioxygen. As such, this represents the initial characterization of an intermediate resulting from O═O bond rupture promoted by a nickel complex.[4a] That the supporting borato ligand contains thioether sulfur donors serves to highlight the utility of this ligand set to stabilize the Ni(I) oxidation state. Facile access to the lower valent species at favorable redox potentials appears advantageous to permit entry to the Ni(I)/Ni(III) couple necessary for $Ni(III)_2(\mu\text{-}O)_2$ formation from dioxygen. Similar two-electron Ni(I)/Ni(III) processes are not accessible in complexes stabilized with nitrogen donor ligands. The ability of the borato ligand to support Ni(I) AND Ni(III) species emphasizes the potential of thioether donors to access the higher oxidation state often deemed the purview of the stronger donor thiolates as found at the active site of NiFe hydrogenases[13] and Ni superoxide dismutase.[14] These results portend the opportunity to further explore and define dioxygen activation using metal complexes supported by thioether sulfur ligation.

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Supporting Information Available: Synthetic details and spectroscopic analyses of new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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