Nickel Compounds

Spectroscopic Elucidation of a Peroxo $Ni_2(\mu\text{-}O_2)$ Intermediate Derived from a Nickel(I) Complex and Dioxygen**

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The preparative chemistry and reactivity of $Ni{-}O_x$ intermediates has advanced significantly in the past few years with the identification of a number of new structure types. The most common synthetic approach, reaction of a nickel(II) precursor with H_2O_2, has yielded bis-μ-oxo[1–4] and bis-μ-superoxo complexes.[4] An attractive alternate route utilizes the reaction of nickel(I) complexes with O_2. This strategy relies on, and is limited by, the ability to prepare suitable nickel(I) species. We have utilized this latter approach to prepare $[\{(PhTt^{tBu})Ni\}_2(\mu\text{-}O)_2]$[5] ($PhTt^{tBu}$ = phenyltris((*tert*-butylthio)methyl)borate) and the related side-on bound superoxo complex, $[\{PhTt^{Ad}\}Ni(O_2)]$ ($PhTt^{Ad}$ = phenyltris((1-adamantylthio)methyl)borate).[6] During the course of these studies, we considered whether a μ-peroxo Ni_2 species was a possible intermediate along the reaction trajectory leading to the bis-μ-oxo dimer. Lacking experimental evidence, a $\mu\text{-}\eta^2,\eta^2$-peroxo bridged Ni_2 dimer supported by the tris(thioether) borato ligand was evaluated by density functional methods.[7] This hypothetical species was deemed to be of high energy, significantly destabilized ($\Delta H° = 32$ kcal mol^{-1}) relative to the bis-μ-oxo dimer and, therefore, an unlikely intermediate. Consequently, we turned our attention to macrocyclic tetradentate ligands that coordinate in a planar array, reasoning that such an attribute would render access to the $\mu\text{-}\eta^2,\eta^2$-peroxo coordination more difficult. Herein, we report on the successful pursuit of this strategy, which led to the discovery of a $Ni_2(\mu\text{-}O_2)$ complex in which the peroxo moiety spans the metals in the μ-1,2 mode.

Addition of dry O_2 to [Ni(tmc)]OTf[8,9] (**1**; tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazadodecane, OTf = $[CF_3SO_3]^-$) in THF or acetonitrile at room temperature resulted in a color change from pale blue to clover green. The FT-IR spectrum of the paramagnetic product ($\mu_{eff} = 2.7(1)\ \mu_B$) included a prominent new feature at 3628 cm^{-1} assigned to the $\tilde{\nu}$(O–H) mode

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[**] Acknowledgement is made to the NSF (CHE-0213260) to C.G.R., and to the University of Wisconsin-Madison to T.C.B. for financial support of this research.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  DOI: 10.1002/ange.200460747

of the $[Ni(tmc)OH]^+$ ion. The assignment of a terminal hydroxy species was confirmed by the independent synthesis of [Ni(tmc)(OH)]OTf (**2**) by metathesis of $[Ni(tmc)](OTf)_2$ and KOH. The $\tilde{\nu}$(O–H) band in the authentic sample of **2** was observed at identical frequency as in the product of the reaction between **1** and O_2. Further, the corresponding ^{1}H NMR spectra are nearly indistinguishable (see Supporting Information). The monomeric nature of **2** was established through X-ray diffraction analysis, Figure 1.[10] The geometry

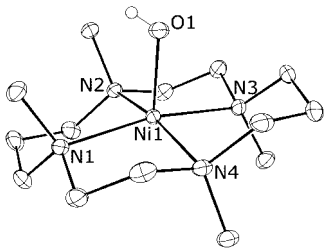


Figure 1. Molecular structure of the cation of **2** derived from an X-ray diffraction analysis. Thermal ellipsoids are set at 30% probability. The hydroxy proton was found in the Fourier difference map.

of the isolated cation is square pyramidal with the amine nitrogen atoms in the basal positions and the terminal hydroxy group in the apical position. The Ni–N bond lengths, which range from 2.116(2) to 2.138(2) Å, are similar to those found for other $[Ni(tmc)X]^+$ species, all of which are high spin, $S = 1$.[9] Compound **2** is the first mononuclear, terminal hydroxy complex of nickel to be defined crystallographically; nonetheless, the Ni–O bond of 1.955(2) Å is consistent with a hydroxy ligand. Further, the hydrogen atom of the hydroxide was found in the difference Fourier map. Isotopic labeling experiments have identified the sources of the hydroxy oxygen and hydrogen atoms in **2**. Addition of $^{18}O_2$ to **1** generated the [Ni(tmc)(^{18}OH)]OTf isotopomer as characterized by a new $\tilde{\nu}(^{18}O–H)$ band at 3617 cm^{-1} ($\tilde{\nu}(^{16}OH)/\tilde{\nu}(^{18}OH) = 1.003$; calcd 1.003 for an isolated harmonic oscillator). Oxygenation of **1** in CD_3CN resulted in isolation of [Ni(tmc)(OD)]OTf (**2^D**) with $\tilde{\nu}$(O–D) at 2677 cm^{-1}, identical in magnitude to **2^D** prepared independently, implicating the solvent as the source of the hydrogen/deuterium. The magnitude of the isotopic shift is smaller than anticipated based on reduced-mass considerations for an isolated harmonic oscillator ($\tilde{\nu}(OH)/\tilde{\nu}(OD) = 1.355$; calcd 1.414).

Low-temperature oxygenation of **1** results in formation of a red intermediate **3**, as indicated by the clean optical progression (isosbestic point at 388 nm, see Supporting Information). In the UV/Vis spectrum, compound **3** is characterized by $\lambda_{max} = 465$ nm (inset Figure 2; $\varepsilon_M = 2100\,M^{-1}cm^{-1}$ per nickel). The intermediate has a limited lifetime at −45 °C in acetonitrile, decaying with $\tau_{1/2} = 4$ min. This thermal instability precludes determination of the Ni:O_2 stoichiometry by spectrophotometric titration. The proton NMR spectrum of **3** in [D_3]acetonitrile shows sharp, paramagnetically shifted resonance signals at 228 K (Supporting Information). Compound **3** is EPR silent between 4 and 77 K. These magnetic data suggest an integer-spin ground state, eliminating the possibility of a 1 Ni:1 O_2 adduct, which would have an $S = 1/2$ or 3/2 ground state. To further elucidate the molecular structure of **3**, resonance Raman (rR) studies were performed. Excitation of **3** in resonance with the visible absorption band ($\lambda_{ex} = 502$ nm) at 77 K revealed two O_2 isotope sensitive features; namely, an intense band at 778 cm^{-1} and a weaker peak at 479 cm^{-1}. These features shift to 735 cm^{-1} and 456 cm^{-1}, respectively, in samples of **3** prepared with $^{18}O_2$ (Figure 2). The frequency and isotopic

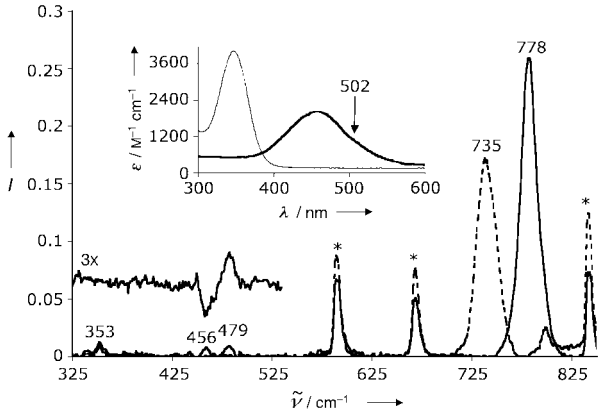
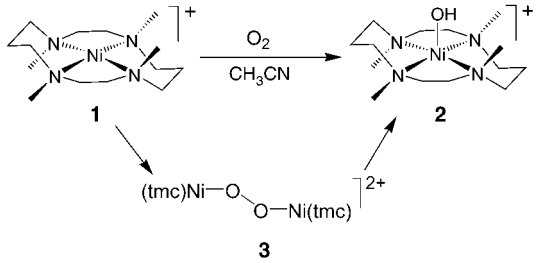


Figure 2. Resonance Raman spectra of **3** at 77 K obtained upon excitation at 502 nm in THF (*); (——) prepared with $^{16}O_2$, (-----) prepared with $^{18}O_2$, offset: Δ($^{16}O_2$ and $^{18}O_2$) traces. Inset: overlaid optical spectra of **1** (-----) and **3** (——).

red-shift (−43 cm^{-1} ($\tilde{\nu}(^{16}O–^{16}O)/\tilde{\nu}(^{18}O–^{18}O) = 1.058$; calcd 1.060 assuming an isolated O–O harmonic oscillator) of the dominant 778 cm^{-1} band are consistent with assignment of this band as an intraperoxide stretch.[11–13] The lower frequency mode is ascribed to the $\tilde{\nu}$(Ni–O) mode associated with this peroxo intermediate, ($\tilde{\nu}(Ni–^{16}O)/\tilde{\nu}(Ni–^{18}O) = 1.050$; calcd 1.048). The rR excitation profile of the 778 cm^{-1} mode closely parallels the dominant absorption band, which leads to the assignment of this absorption band as a peroxo→Ni^{2+} charge transfer (CT) transition. Together with the magnetic properties, the rR features are indicative of a dimeric μ-1,2-peroxo formulation for **3** (Scheme 1).[14] We favor the *trans* conformation because this core structure is generally adopted by other unsupported peroxo-bridged species. Comparison with vibrational data of other *trans* end-on peroxo dimers lends credence to this assignment. In particular, in [{Cu(tmpa)}$_2$(O_2)]$^{2+}$ (tmpa = tris(2-methylpyridyl)amine)) the $\tilde{\nu}$(O–O) and $\tilde{\nu}$(Cu–O) stretching vibrations are at 832 cm^{-1} and 561 cm^{-1}, respectively.[12] The frequency of $\tilde{\nu}$(M–O) vibration



Scheme 1.

is slightly lower than found in *trans* μ-1,2-peroxo dimers of copper(II) and cobalt(III)[15] which is consistent with a weaker (that is, less covalent) metal–peroxo bonding interaction in the Ni_2 dimer owing primarily to the lower effective nuclear charge of nickel(II) relative to copper(II) and cobalt(III). Also, **3** differs from these other late-transition-metal examples in that the nickel center does not have a ligand *trans* to the peroxo group, as evidenced by the identical optical spectra of **3** in THF and CH_3CN, thus arguing against solvent ligation to the sixth coordination site. This lack of a *trans* axial ligand in **3** eliminates the possibility of mechanical coupling between the Ni–O and Ni–L_{trans} stretching motions, which otherwise could lead to a slight upshift of the $\tilde{\nu}$(Ni–O) vibration. The relative intensities of the Ni–O and O–O vibrational modes, specifically the extreme enhancement of $\tilde{\nu}$(O–O), strongly suggest that the kinematic coupling between the oxygen-derived modes is substantial. DFT computational studies and a normal coordinate analysis of **3** are underway to elucidate further the nature of the $Ni_2(\mu\text{-}O_2)$ unit and determine the factors that control the electronic and vibrational characteristics of this new chromophore.

In summary, we have identified a binuclear *trans*-μ-1,2-peroxo Ni_2 dimer, a structural motif unknown previously in nickel coordination chemistry, produced by reaction of a nickel(I) precursor with O_2. This structural assignment of **3** is supported by EPR, NMR, and rR spectral characteristics as well as DFT computations. Thermal decomposition of **3** in CH_3CN leads to **2**, in which the atoms constituting the hydroxide ligand derive from O_2 and the hydrocarbon solvent.

Experimental Section

2: Potassium hydroxide pellets (1.30 g, excess) were added to a slurry of [Ni(tmc)](OTf)$_2$[16] (380 mg, 0.619 mmol) in THF (≈15 mL). The mixture was stirred for 1 h, resulting in a homogeneous green solution. The mixture was filtered to remove the remaining KOH, and the product was crystallized by diethyl ether vapor diffusion; 81% yield (0.240 g, 0.499 mmol). Green crystals suitable for diffraction analysis were obtained by vapor diffusion of pentanes into a saturated THF solution. Elemental analysis calcd (%) for $N_4O_{4.6}SNiC_{15}F_3H_{34.3}$ (**2**·(2/3)H_2O): C 36.53, H 7.02, N 11.36; found: C 37.09, H 6.90, N 11.24. FT-IR (Nujol): $\tilde{\nu}$(OH) 3628 cm^{-1} (w). Electronic absorption spectrum in MeCN, $\lambda_{max}(\varepsilon_M)$: 409 (41.4), 657 nm (30.1).

2^D: Potassium deuteroxide (KOD) was prepared from the reaction of potassium *tert*-butoxide (1.96 g, 17.5 mmol) with D_2O (5 mL, excess). Excess water and [D_1]*tert*-butanol were removed in vacuo overnight. **2^D** was prepared by a method analogous to that for **2**, using KOD in place of KOH and CD_3CN instead of THF. FT-IR (Nujol): $\tilde{\nu}$(OD) 2677 cm^{-1} (w).

Received: May 23, 2004
Revised: August 4, 2004
Published online: November 19, 2004

Keywords: coordination modes · N ligands · nickel · oxygen · structure elucidation

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[10] X-ray structural analysis for **2**: A single green crystal (0.40 × 0.20 × 0.15 mm) was mounted using Paratone oil onto a glass fiber and cooled to the data collection temperature of 150 K. Data were collected on a Bruker-AXS APEX CCD diffractometer with 0.7107 Å $Mo_{K\alpha}$ radiation. Unit cell parameters were obtained from 60 data frames, 0.3° Ω, from three different sections of the Ewald sphere yielding $a = 12.163(4)$, $b = 12.660(4)$, $c = 14.104(5)$ Å, $\alpha = 86.715(6)$, $\beta = 80.626(5)$, $\gamma = 89.312(5)°$, $V = 2139.1(12)$ Å^3. 14169 reflections ($R_{int} = 0.0117$) were collected (8939 unique) over $\theta = 2.05$ to 28.02°. No symmetry higher than triclinic was evident from the diffraction data. Solution in the centrosymmetric space group option $P\bar{1}$ yielded chemically reasonable and computationally stable results of refinement. The data-set was treated with SADABS absorption corrections based on redundant multiscan data (G. Sheldrick, Bruker-AXS, 2001) $T_{max}/T_{min} = 1.268$. A molecule was located in a general position while two-half molecules were also located at inversion centers yielding $Z = 2$, and $Z' = 2$. The molecule in general space has a coordinated hydroxide ligand on one metal face and a noncoordinated water molecule on the opposite face. The hydrogen atom on the hydroxy ligand was located from the electron-density-difference map and allowed to refine positionally with a riding isotropic model. The other symmetry unique molecules were assumed to be chemically identical and having water molecules disordered with hydroxy ligands. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions except those on the disordered hydroxy ligands and water molecules which were ignored. Structure factors are contained in the SHELXTL 6.12 program library (Sheldrick, G., Bruker-AXS, 2001). The goodness of fit on F^2 was 1.054 with $R1(wR2)$ 0.0348 (0.0905) for [$I\theta > 2(I)$] and with largest difference peak and hole of 0.776 and −0.466 e Å^{-3}. CCDC-238390 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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