Inorg. Chem. **2002**, *41*, 2307–2309

Inorganic Chemistry
Communication

Oxygen Reactivity of a Nickel(II)–Polyoximate Complex

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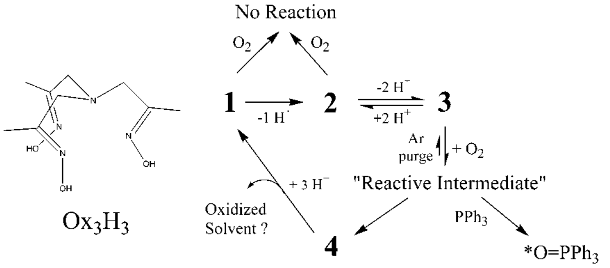
Received September 21, 2001

The ligand tris(2-hydroxyiminopropyl)amine (Ox_3H_3) binds to nickel(II) in multiple protonation states. In the neutral state, the X-ray crystal structure of the monomeric complex $[Ni(Ox_3H_3)(NO_3)(H_2O)](NO_3)\cdot(H_2O)$, **1**, has six-coordinate pseudo-octahedral geometry, with binding of the amine and three oxime nitrogens, a nitrate, and a water. In the mono-deprotonated form, the X-ray crystal structure shows a dimer, $[Ni(Ox_3H_2)(CH_3CN)]_2(ClO_4)_2$, **2**, which has bridging oximate groups and a Ni–Ni distance of 3.575 Å. The fully deprotonated complex, **3**, shows significantly low Ni(II) oxidation potentials at –390 and +165 mV (versus Fc^+/Fc). Complex **3** shows reactivity when exposed to O_2, consuming multiple O_2 equivalents and turning from the purple **3** to a dark brown complex, **4**. Complex **4** has an EPR spectrum consistent with Ni(III), but spin quantitation accounts for only about 10% of the total Ni, consistent with turnover of the Ni oxidation states. This Ni(II)/O_2 system oxidizes triphenylphosphine to its oxide, with incorporation of the isotopic label from O_2.

Reactions of dioxygen catalyzed by metals are significant in a number of industrial[1] and biological[2] syntheses. Thus, the development of new oxygen activation catalysts is of great interest. Nickel(II) complexes are usually inactive toward O_2 due in part to the inaccessibility of the higher oxidation states, Ni(III) and Ni(IV). A few cases of O_2 reactions with Ni(II)−amidate complexes are reported[3] in which ligand degradation occurs, likely due to a one-electron reduction of O_2 to a superoxo-like intermediate.[4] Oxygen reactions of Ni(II)−thiolate complexes show oxidation of the sulfur rather than the nickel.[5] We are investigating Ni complexes of ligands that incorporate oximate donors,[6] which have been shown to stabilize the Ni(III) and Ni(IV) oxidation states at low potential.[7] Here we report the large structural and electrochemical differences between Ni(II) complexes of the ligand tris(2-hydroxyiminopropyl)amine[8] (Ox_3H_3) in different protonation states (shown in Scheme 1). The deprotonated complex is oxidized by O_2, and this system oxidizes PPh_3, with incorporation of oxygen from O_2. This reactivity distinguishes this complex from recently reported $Ni^{III}_2(\mu\text{-}O)_2$ complexes.[9] These have been reported to form from a reaction of a Ni(I)−thioether complex with O_2[10] and by reaction of Ni(II) complexes with H_2O_2.[9,11]

Scheme 1. Ligand Structure and Deprotonation and Reactivity of the Ni(II) Complexes



Addition of the neutral ligand Ox_3H_3 to $Ni^{II}(NO_3)_2\cdot 6H_2O$ gives a purple six-coordinate complex, **1**, $[Ni(Ox_3H_3)(NO_3)$-

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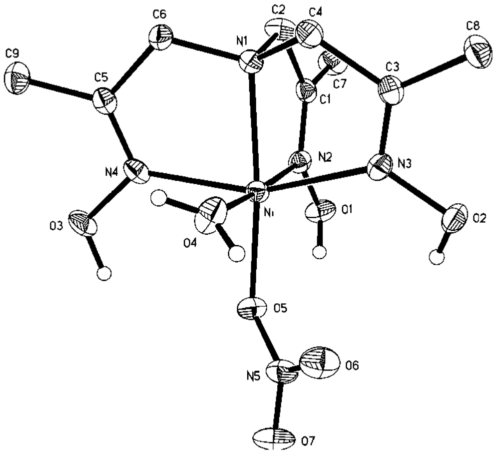

Figure 1. X-ray crystal structure of **1**, $[Ni(Ox_3H_3)(NO_3)(H_2O)](NO_3)\cdot(H_2O)$, with nitrate anion omitted.

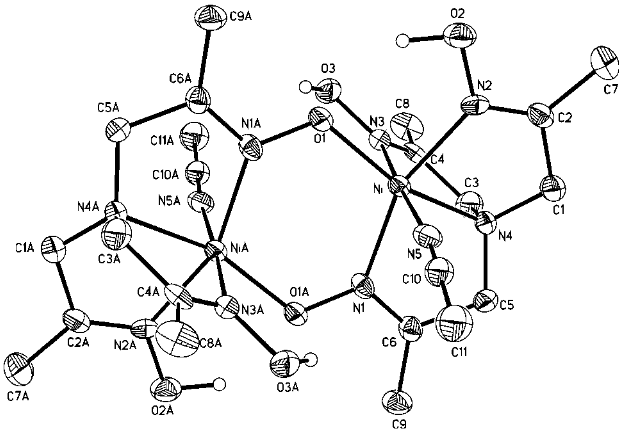

Figure 2. X-ray crystal structure of **2**, $[(Ni(Ox_3H_2)(CH_3CN)]_2(ClO_4)_2$, with perchlorate anions omitted.

$(H_2O)](NO_3)\cdot(H_2O)$, shown in Figure 1. The ligand binds through the amine and three oxime nitrogens. In the solid, nitrate and water occupy the other two coordination positions. Partial deprotonation of **1** in CH_3CN yields the purple complex **2**, $[Ni(Ox_3H_2)(CH_3CN)]_2(ClO_4)_2$, shown in Figure 2. This compound is a $Ni(II)_2$ dimer, in which one oxime group from each ligand/Ni unit is deprotonated to form a μ(N−O) bridge,[12] while two neutral oximes, the amine, and acetonitrile coordinate to each nickel through their nitrogens. The Ni−Ni distance is 3.575 Å.

Addition of 3 equiv of hydroxide to **1** (in an Ar atmosphere) yields complex **3**. The oxidation potentials of **3** are significantly lower than those of other Ni(II) complexes with typical donor groups, such as amines. Complexes **1** and **2** show only irreversible oxidations above +500 mV (versus Fc^+/Fc). The cyclic voltammogram of **3** (Figure 3) shows major oxidation waves at −390 mV (quasireversible, $E_{1/2} = -440$ mV, $\Delta E = 100$ mV) and +165 mV (irreversible), versus Fc^+/Fc (the rest potential is −515 mV). Coulometry shows that oxidation of the complex at just above the lower oxidation potential transfers one electron per nickel. This suggests that the first wave at −390 mV is an oxidation in which all of the Ni(II) species are oxidized to Ni(III), and the second wave at +165 mV is likely a Ni(III) to Ni(IV) oxidation.

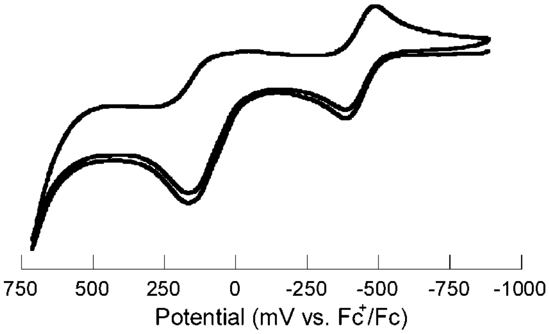

Figure 3. Cyclic voltammogram of **3** in CH_3CN (100 mM Bu_4NPF_6), 150 mV/s. Potentials are referenced versus Fc^+/Fc under the same experimental conditions. The rest potential is −515 mV.

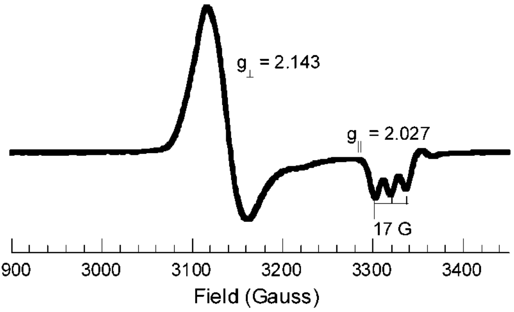

Figure 4. X-band EPR spectrum of the air-oxidized (4 h exposure) complex **4**, 100 K in methanol.

While compounds **1** and **2** are insensitive to O_2, both solutions and solids of complex **3** react with O_2. Exposure of a purple solution of **3** to air or O_2 gas results in the formation of a brown complex, **4**. Immediate purging of the reaction with argon shows nearly reversible regeneration of the purple complex **3**. Subsequent exposures to O_2 followed by purging with argon can be followed by UV/vis spectroscopy (Figure S11 in Supporting Information) and show cycling of the O_2 reaction. Long exposures to O_2 result in loss of reversibility of the reaction. Manometry shows consumption of 7−8 equiv of O_2 per Ni before uptake eventually stops. Addition of acid to **4** returns complex **1**, likely by oxidation of solvent after reprotonation of the oximes.

The EPR spectrum of the air/O_2 oxidized nickel complex is consistent with a Ni(III) monomer,[13] with $g_\perp = 2.143$ and $g_\| = 2.027$ (Figure 4). However, quantitation of the EPR signal accounts for only about 10% of the Ni. This may be explained by a steady state concentration of Ni(III) in the solution resulting from O_2 oxidation, which oxidizes a substrate (such as solvent) to return to Ni(II), consistent with the uptake of multiple equivalents of O_2. This is further supported by comparison of the UV/vis absorption spectra of the air and the electrochemically oxidized solutions. The spectra are similar, but the intensity of the characteristic

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absorption band at 540 nm in the air-oxidized solution is only about $^1/_{10}$ the intensity of that of the electrochemically oxidized sample. This EPR spectrum is likely to correspond not to the initial, reactive Ni species, but rather to a more slowly reduced product of its reaction with solvent.

Addition of excess PPh_3 to the reaction of **3** with $^{16}O_2$ in methanol yields 2 equiv (per Ni) of the oxidized product, triphenylphosphine oxide (reaction of **1** or **2** with PPh_3 and O_2 yields no oxide). The same reaction with $^{18}O_2$ shows nearly complete incorporation of the labeled oxygen into the triphenylphosphine oxide, even with addition of 20 equiv of $H_2{}^{16}O$ to the solvent.[14] This is consistent with transfer of an oxygen atom from a nickel-bound active oxygen species derived from O_2. In contrast, initial one-electron oxidation of PPh_3 by a high-valent Mn complex results in reaction with water to produce the oxide with the isotopic label from trace water in the solvent rather than from O_2.[15] The oxygen reactivity of a $Ni^{III}{}_2(\mu\text{-}O)_2$ dimer reported by Itoh[11] shows only hydrogen atom abstraction type chemistry, but no oxygen atom transfer reactivity. Additionally, the copper–oxygen systems reported by Stack[16] and Tolman[17] show that $Cu^{III}{}_2(\mu\text{-}O)_2$ complexes oxidize substrates by hydrogen atom abstraction, but $Cu^{II}{}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2{}^{2-})$ complexes preferentially perform oxygen atom transfer. This analogy suggests that the reactive species in the Ni(II)–oximate/O_2 system has reactivity similar to that of the copper–peroxo systems.

In summary, the ligand tris(2-hydroxyiminopropyl)amine coordinates to Ni(II) in multiple protonation states, forming monomers and oximate-bridged dimers. The Ni(II) complex of the fully deprotonated ligand has low oxidation potentials and reacts with O_2, with uptake of multiple O_2 equivalents. This reaction promotes O_2 oxidation of an oxygen atom transfer substrate, PPh_3, with incorporation of labeled oxygen. This ligand and related polyoximates provide a new class of oxygen-active Ni(II) complexes. Further characterization of complexes **3** and **4**, screening for oxidation of other potential substrates, and study of the O_2 reaction mechanism are ongoing.

Acknowledgment. Funding was provided by the Petroleum Research Fund administered by the American Chemical Society (ACS-PRF 33960-G3) and the University of Cincinnati. We also thank Prof. Gary Lorigan and Thomas Cardon at Miami University for assistance in collection of EPR data (EPR instrument funded by NSF CHE-97,24192), the Ohio Crystallographic Consortium located at the University of Toledo, and the Ohio Mass Spectrometry Consortium at the University of Cincinnati.

Supporting Information Available: Experimental details about the synthesis and characterization of Ox_3H_3, **1**, and **2**, and reactions of **3**, FTIR, EPR, UV/vis, mass spectral, and electrochemical data, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The IR spectrum of the ^{16}O oxide product shows the $\nu(P{=}O)$ band at 1189 cm^{-1}, and the mass spectrum shows an M + 1 peak at $m/z = 279$. The IR spectrum of the ^{18}O oxide product shows $\nu(P{=}O)$ at 1150 cm^{-1} and M + 1 at $m/z = 281$.

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