Nickel(III) Complexes

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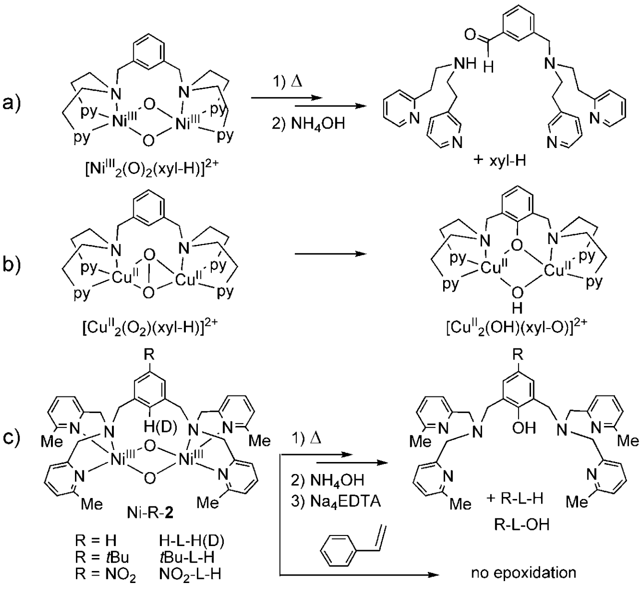
Oxidation Reactivity of Bis(μ-oxo) Dinickel(III) Complexes: Arene Hydroxylation of the Supporting Ligand**

*Kaoru Honda, Jaeheung Cho, Takahiro Matsumoto, Jungyun Roh, Hideki Furutachi, Takehiko Tosha, Minoru Kubo, Shuhei Fujinami, Takashi Ogura, Teizo Kitagawa, and Masatatsu Suzuki**

M$_2$/O$_2$ complexes capable of hydroxylating arenes have attracted much attention as functional models for dioxygen-activating dimetal enzymes such as tyrosinase ({Cu$_2$O$_2$}) and toluene monooxygenase ({Fe$_2$O$_2$}). Tyrosinase has been shown to generate a μ-η^2:η^2-peroxo dicopper(II) species as an active intermediate for hydroxylation of phenol to catechol.[1–3] Recently, a peroxo diiron(III) intermediate was discovered in toluene/*o*-xylene monooxygenase, which directly oxidizes phenol to catechol.[4] In addition to these peroxo dimetal species, model studies have revealed that some bis(μ-oxo) dicopper(III) species[5] are also capable of hydroxylating arenes, as are μ-η^2:η^2-peroxo dicopper(II) complexes.[6] Oxidation reactivities that depend on the oxidant types in M$_2$/O$_2$ chemistry, such as peroxo versus bis(μ-oxo) dimetal species, are of particular interest.

Itoh and co-workers have demonstrated that a bis(μ-oxo) dinickel(III) complex bearing a xyl-H ligand, [Ni$_2$(O)$_2$(xyl-H)]$^{2+}$ (Scheme 1 a), exhibits N-dealkylation by H-atom abstraction from a methylene group of xyl-H,[7a] which is in marked contrast to the hydroxylation of the xylyl linker of xyl-H by the μ-η^2:η^2-peroxo dicopper(II) complex [Cu$_2$(O$_2$)-(xyl-H)]$^{2+}$ (Scheme 1 b) reported by Karlin and co-workers.[6a,b] Oxidation reactions of C–H bonds mediated by the bis(μ-oxo) dinickel(III) complexes reported to date have been shown to proceed by H-atom abstraction.[7–10] No arene hydroxylation by a bis(μ-oxo) dinickel(III) species has been reported.[11,12]



Scheme 1. Oxidation reactivity of μ-η^2:η^2-peroxo dicopper(II) and bis-(μ-oxo) dinickel(III) complexes bearing dinucleating ligands. EDTA = ethylenediaminetetraacetate.

Recently we found that the μ-η^2:η^2-peroxo dicopper(II) complex [Cu$_2$(O$_2$)(H-L-H)]$^{2+}$ (Cu-H-**2**, H-L-H = 1,3-bis-[bis(6-methyl-2-pyridylmethyl)aminomethyl]benzene) is capable of hydroxylating the xylyl linker of H-L-H and epoxidizing styrene.[6e,f] Thus, it is of particular interest to investigate the oxidation reactivity of bis(μ-oxo) dinickel(III) complexes with R-L-H ligands ([Ni$_2$(O)$_2$(R-L-H)]$^{2+}$, Ni-R-**2**, Scheme 1 c) in comparison to [Cu$_2$(O$_2$)(R-L-H)]$^{2+}$. Herein, we report arene hydroxylation by bis(μ-oxo) dinickel(III) complexes bearing R-L-H ligands.

Reaction of a green acetonitrile solution of the bis(μ-hydroxo) dinickel(II) complex [Ni$_2$(OH)$_2$(H-L-H)]$^{2+}$ (Ni-H-**1**) with one equivalent H$_2$O$_2$ at −40 °C generated a brown species. The electronic absorption spectrum of the brown solution at −40 °C (Figure 1) exhibits an intense absorption band at 409 nm ($\varepsilon \geq 3800\,\text{M}^{-1}\text{cm}^{-1}$, estimated from the maximum absorbance, as the brown species was not stable and formation and decomposition occurred simultaneously).[13] Spectroscopic titration (Figure 1, each data point was measured in a separate experiment) to monitor the

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[*] K. Honda, Prof. Dr. J. Cho,[+] Dr. T. Matsumoto, J. Roh,
Dr. H. Furutachi, Prof. S. Fujinami, Prof. M. Suzuki
Department of Chemistry
Graduate School of Natural Science and Technology
Kanazawa University, Kakuma-machi, Kanazawa 920-1192 (Japan)
Fax: (+81) 76-264-5742
E-mail: suzuki@cacheibm.s.kanazawa-u.ac.jp
Homepage: http://chem.s.kanazawa-u.ac.jp/coord/index.html
Dr. T. Tosha, Prof. T. Kitagawa
Okazaki Institute for Integrative Bioscience
National Institutes of Natural Sciences
Myodaiji, Okazaki, 444-8787 (Japan)
Dr. M. Kubo, Prof. T. Ogura
Picobiology Institute, Graduate School of Life Science
University of Hyogo, Ako-gun, Hyogo 678-1297 (Japan)

[+] Current address: Department of Chemistry and Nano Science
Ewha Womans University, Seoul 120-750 (Korea)

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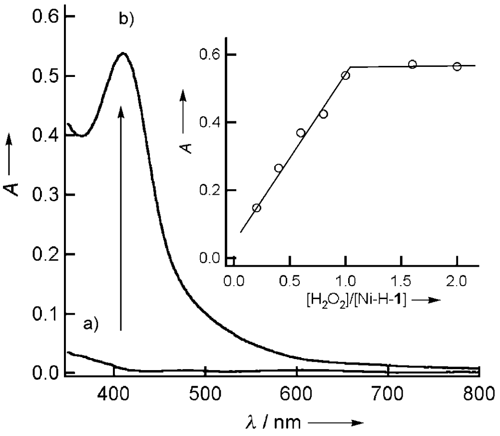

Figure 1. Electronic spectra of a) $[Ni_2(OH)_2(H\text{-}L\text{-}H)]^{2+}$ (Ni-H-**1**) and b) $[Ni_2(O)_2(H\text{-}L\text{-}H)]^{2+}$ (Ni-H-**2**) generated in the reaction of Ni-H-**1** (0.132 mM) with one equivalent H_2O_2 (19.5 mM) prepared by dilution of 30% H_2O_2 in acetonitrile at −40 °C. Spectrum (b) was measured 300 s after addition of H_2O_2 (optical path length = 1.06 cm). Inset is the spectroscopic titration at 409 nm for the stepwise formation of Ni-H-**2** by addition of H_2O_2 to an acetonitrile solution of Ni-H-**1** at −40 °C.

formation of the brown species revealed that one equivalent H_2O_2 is needed for full formation. The spectral feature at 409 nm is quite similar to those of five-coordinate bis(μ-oxo) dinickel(III) complexes containing tridentate N donors ($\lambda_{max} = 405$–414 nm).[7,8] The resonance Raman (rR) spectrum of the brown solution prepared by $H_2{}^{16}O_2$ showed a band at 616 cm^{-1}, which shifted to 587 cm^{-1} when $H_2{}^{18}O_2$ was used (Figure 2). The band can be assigned as a Ni_2O_2 core vibration typical of bis(μ-oxo) dinickel(III) complexes bearing tridentate nitrogen donors (599–612 cm^{-1}).[7,8] Thus the brown species can be assigned as the bis(μ-oxo) dinickel(III) complex $[Ni(O)_2(H\text{-}L\text{-}H)]^{2+}$ (Ni-H-**2**). Similar rR and UV/Vis spectral features were also observed for Ni-H-**2**(D), Ni-*t*Bu-**2**, and Ni-NO_2-**2** (Figures S1 and S2 in the Supporting Information). The formation of the bis(μ-oxo) dinickel(III) species by O–O bond cleavage is in contrast to the existence of μ-η^2:η^2-peroxo dicopper(II) complex Cu-H-**2**. This difference arises because the nickel species can more easily access a higher oxidation state than the corresponding copper complexes, owing to the higher d-orbital energy of the nickel complexes.[14]

The ESI-TOF mass spectrum of Ni-H-**2** in acetonitrile showed a signal at *m*/*z* 352.1 together with some unidentified signals (Figure S3 in the Supporting Information). The 352.1 signal can be assigned as $[Ni_2(O)_2(H\text{-}L\text{-}H)]^{2+}$ (Ni-H-**2**) or $[Ni_2(OH)(H\text{-}L\text{-}O)]^{2+}$ (Ni-H-**3**), which has a hydroxylated ligand (H-L-O; Scheme 1 c). The ESI-TOF mass spectrum of a sample produced by $H_2{}^{18}O_2$ showed a signal at *m*/*z* 353.1, indicating the presence of only one ^{18}O atom. Furthermore, addition of methanol caused the shift of the signal at *m*/*z* 352.1 to 359.1 for an ^{16}O sample and the shift of the signal at *m*/*z* 353.1 to 360.1 for an ^{18}O sample, indicating the presence of OH^-. The results are consistent with formation of Ni-H-**3** under the ESI-TOF mass spectrometry conditions, and the oxygen atom of the hydroxylated ligand H-L-O comes from H_2O_2. Product analysis of decomposed Ni-H-**2** in acetonitrile (the sample stood for 24 h under N_2 at −40 °C) revealed the hydroxylation of the xylyl linker of H-L-H to produce H-L-OH, which was identified using NMR spectroscopy by comparison with authentic H-L-OH (see the Supporting Information). Ni-*t*Bu-**2** and Ni-NO_2-**2** also generated the corresponding hydroxylated ligands upon decomposition. The yields of *t*Bu-L-OH, H-L-OH, and NO_2-L-OH are 88–78, 67–60, and 37–30%, respectively (Figures S4–S6 in the Supporting Information). Thus, unlike $[Ni_2(O)_2(xyl\text{-}H)]^{2+}$,[7a] Ni-R-**2** is capable of hydroxylating the xylyl linker of R-L-H, as found for the corresponding μ-η^2:η^2-peroxo dicopper(II) complexes.

To gain further insight into the hydroxylation mechanism, thermal decomposition of Ni-R-**2** and the complex $[Ni_2(O)_2(H\text{-}L\text{-}D)]^{2+}$ (Ni-H-**2**(D)) bearing a ligand H-L-D substituted with deuterium at the hydroxylated position was monitored using the spectral change at 409 nm in acetonitrile at −40–0 °C.[13] Decomposition of Ni-R-**2** and Ni-H-**2**(D) obeyed a first-order rate law ($v = k$[Ni-R-**2**] or $v = k$[Ni-H-**2**(D)]), thus indicating that the decomposition is a unimolecular process (Figure S2 and Table S1 in the Supporting Information). No measurable kinetic deuterium isotope effect (k_H ($2.9 \times 10^{-4}\ s^{-1}$)/$k_D$ ($2.8 \times 10^{-4}\ s^{-1}$) ≈ 1 for Ni-H-**2** and Ni-H-**2**(D) at −40 °C, Figure 3) was observed, thus indicating that the rate-determining step does not involve H-atom abstraction from the xylyl linker. A similar observation was also made for the hydroxylation reactions mediated by μ-η^2:η^2-peroxo dicop-

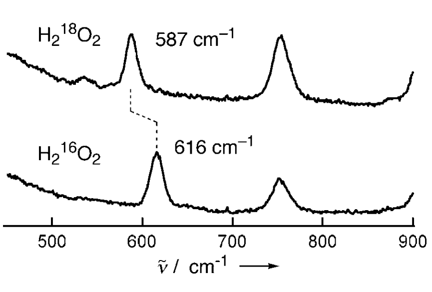

Figure 2. Resonance Raman spectra of $[Ni_2(O)_2(H\text{-}L\text{-}H)]^{2+}$ (Ni-H-**2**) generated in the reaction of $[Ni_2(OH)_2(H\text{-}L\text{-}H)]^{2+}$ (Ni-H-**1**) with $H_2{}^{16}O_2$ or 2% aqueous $H_2{}^{18}O_2$ in acetonitrile at −40 °C (406.7 nm laser excitation).

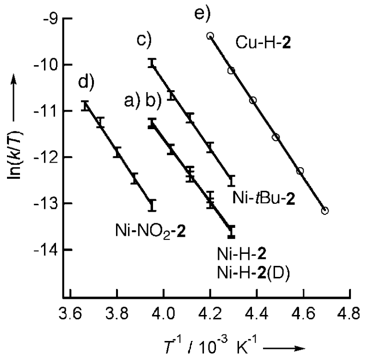

Figure 3. Comparison of the Eyring plots of thermal decompositions for a) Ni-H-**2**, b) Ni-H-**2**(D), c) Ni-*t*Bu-**2**, d) Ni-NO_2-**2**, and e) Cu-H-**2**.

per(II) complexes $[Cu_2(O_2)(H\text{-}L\text{-}H)]^{2+}$ and $[Cu_2(O_2)(H\text{-}L\text{-}D)]^{2+}$ (Cu-H-**2** and Cu-H-**2**(D)).[6e] Ni-H-**2** is approximately 30 times less reactive than the corresponding μ-η^2:η^2-peroxo dicopper(II) complex ($k = 2.9\times10^{-4}\,s^{-1}$ for Ni-H-**2** and $k = 9.4\times10^{-3}\,s^{-1}$ for Cu-H-**2**) at −40 °C (Table S2 in the Supporting Information). Such lower reactivity can be attributed to an unfavorable activation entropy change for Ni-H-**2** ($\Delta H^{\neq} \approx 59\,kJ\,mol^{-1}$ and $\Delta S^{\neq} \approx -56\,J\,mol^{-1}\,K^{-1}$) compared to that of Cu-H-**2** ($\Delta H^{\neq} = 63\,kJ\,mol^{-1}$ and $\Delta S^{\neq} = -11\,J\,mol^{-1}\,K^{-1}$).[6e] The results suggest that the transition state of the reaction involving Ni-H-**2** is highly ordered compared to that of Cu-H-**2**. Such lower oxidation reactivity of nickel complexes compared to corresponding copper complexes bearing the same ligand system has also been observed for bis(μ-oxo) M_2(III) complexes (M = Cu and Ni) $[M_2(O)_2(Me_n\text{-}tpa)_2]^{2+}$ ($n = 2$ and 3, Me_2-tpa = bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine and Me_3-tpa = tris(6-methyl-2-pyridylmethyl)amine).[9,10,15]

It should also be noted that the decomposition rates of Ni-R-**2** depend on the electron-donating power of the substituent R of H-R-H (Figure 3). Stronger electron donation from substituent R increases the decomposition rate of Ni-R-**2**.[16] A similar observation was also made for a series of μ-η^2:η^2-peroxo dicopper(II) complexes Cu-R-**2**,[6e] suggesting that hydroxylation reactions of Ni-R-**2** also proceed by electrophilic aromatic substitution. This finding is in line with the lack of kinetic deuterium isotope effect mentioned above.

We also studied epoxidation of styrene (1.45 M) by Ni-H-**2** (0.83 mM) in acetonitrile at −40 °C. Unlike the epoxidation ability of Cu-H-**2**,[6e] Ni-H-**2** is not capable of oxidizing styrene. Only hydroxylation of the xylyl linker of H-L-H was observed. This difference is probably due to lower oxidation reactivity of Ni-H-**2** toward the external substrate compared to Cu-H-**2**, as mentioned above, and/or to the smaller reaction cavity of Ni-H-**2** which prevents a close approach of styrene to the bis(μ-oxo) Ni^{III}_2 core, since the Ni···Ni distance in Ni-H-**2** must be shorter than the Cu···Cu distance of Cu-H-**2**.

In summary, we have demonstrated arene hydroxylation by bis(μ-oxo) dinickel(III) complexes Ni-R-**2**. Kinetic studies strongly suggest that the hydroxylation proceeds by an electrophilic aromatic substitution mechanism, as found for the corresponding μ-η^2:η^2-peroxo dicopper(II) complexes Cu-R-**2**.

Experimental Section

$[Ni_2(OH)_2(H\text{-}L\text{-}H)](ClO_4)_2\cdot 0.5\,EtOH\cdot 0.5\,H_2O$ (Ni-H-**1**$\cdot 2\,ClO_4\cdot 0.5\,EtOH\cdot 0.5\,H_2O$): The complex was prepared under N_2 using Schlenk techniques. Solid $Ni(ClO_4)_2\cdot 6\,H_2O$ (0.366 g, 1 mmol) was dissolved in an ethanol solution (30 mL) of H-L-H (0.278 g, 0.5 mmol) to give a green solution, to which was added triethylamine (0.101 g, 1 mmol) to yield a green precipitate. The green precipitate was collected by filtration and washed with diethyl ether and dried in vacuo. Yield: 0.704 g (75 %). UV/Vis (acetonitrile): λ_{max} (ε) = 480 (24) and 617 nm ($28\,M^{-1}\,cm^{-1}$); FTIR (KBr, cm^{-1}): $\tilde{\nu} = 3415$ (w; O−H), 1608 (m; C=C, aromatic), 1577 (m; C=C, aromatic), 1111 (s; ClO_4^-), 627 cm^{-1} (s; ClO_4^-); ESI-MS (acetonitrile): m/z (%): 353.1 (100) [M^{2+}]; elemental analysis (%) calcd for $C_{37}H_{46}N_6Ni_2Cl_2O_{11}$: C 47.32, H 4.94, N 8.95; found: C 47.51, H 5.22, N 8.68.

Synthesis of other complexes and details of experiments including kinetic studies are given in the Supporting Information.

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[16] Although the yield of hydroxylation reaction of Ni-NO_2-**2** (37–30%) is poor, the slow decomposition rate indicates that the hydroxylation rate slows down owing to the poor electron-donating power of the NO_2 group and some other side reaction (or reactions) that takes place simultaneously. In this study, however, we could not identify such a side reaction.