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Aliphatic Hydroxylation by a Bis(μ-oxo)dicopper(III) Complex**

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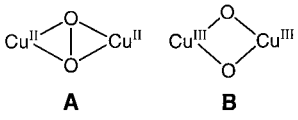
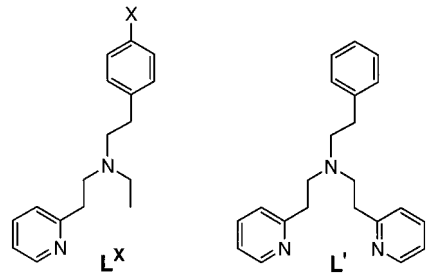
Understanding how metal – dioxygen adducts react in biochemical and synthetic transformations of organic substrates is an important research objective.[1] Significant progress toward this goal has been made through the detailed characterization of complexes derived from the reaction of dioxygen with Cu^I precursors.[2] Of the adducts characterized by X-ray crystallography to date[3–5] the (μ-η^2:η^2-peroxo)- and bis(μ-oxo)dicopper units **A** and **B**, respectively, have drawn particular attention as a consequence of their known or potential relevance to intermediates in hydroxylation reactions performed by copper oxygenases such as tyrosinase and particularly methane monooxygenase (pMMO).[6] Although **B** has yet to be observed in an enzyme system, the possibility that **A** (identified as an intermediate in tyrosinase and catechol oxidase) may convert into **B** prior to activation of the substrate C–H bond is supported by the observed reactivity of synthetic examples of these cores.[5, 7, 8] Evidence in support of the ability of core **B** to hydroxylate arene rings,[9] to abstract H atoms from the weak C–H bonds of dihydroanthracene,[10] and to oxidatively N-dealkylate ligand substituents has been uncovered.[5, 11] Mechanistic studies of the latter reaction implicate an initial hydroxylation at the activated position α to the N donor by a rate-controlling C–H bond scission to yield a presumed carbinolamine intermediate, which then decays to the product aldehyde and secondary amine.[11] However, direct observation of the hydroxylation of aliphatic C–H bonds by **B**, a reaction relevant to the function of monooxygenase (for example, pMMO), has remained elusive.[12]



Herein we describe a new set of bis(μ-oxo)dicopper complexes with ligand $\mathbf{L^X}$ ($\mathbf{L^X}$ = *p*-substituted *N*-ethyl-*N*-[2-(2-pyridyl)ethyl]-2-phenylethylamine; X = OMe, Me, H, Cl, NO_2) that decompose to a product in which the ligand is hydroxylated at its benzylic position. Detailed characterization of this newly discovered aliphatic C–H bond activation reaction by core **B** reveals important information on the fundamental chemistry underlying copper monooxygenase reactivity.



(X = OMe, Me, H, Cl, NO_2)

Figure 1 shows the spectral changes observed upon introduction of O_2 into a solution of $[Cu^I(\mathbf{L^H})(CH_3CN)]PF_6$ in acetone at $-90\,^\circ C$.[13] An absorption band at 402 nm (ε = 17700 $M^{-1}cm^{-1}$)[14] similar to those of the bis(μ-oxo)dicopper(III) complexes reported previously[5] appears gradually. Also similar to other complexes with core **B** is that the solution is ESR silent. Furthermore, the resonance Raman spectrum (λ_{ex} = 457.9 nm) of a frozen [D_6]acetone solution of the intermediate generated using $[Cu^I([D_4]\mathbf{L^H})(CH_3CN)]PF_6$ ([D_4]$\mathbf{L^H}$: *N*-ethyl-*N*-[2-(2-pyridyl)ethyl]-1,1,2,2-tetradeuterio-2-phenylethylamine) has an intense peak at 607 cm^{-1} that shifts to 578 cm^{-1} upon isotopic substitution with $^{18}O_2$ (see inset of Figure 1). This frequency and isotopic shift ($\Delta\tilde{\nu}$ = 29 cm^{-1}) are very close to those reported for bis(μ-oxo)di-

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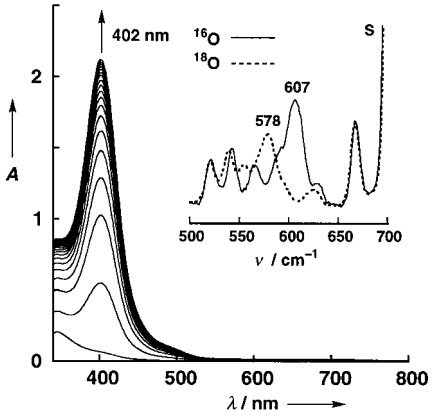


Figure 1. Changes in the UV/Vis spectrum observed at 5 s intervals upon introduction of O_2 gas into an acetone solution of $[Cu^{I}(\mathbf{L^H})(CH_3CN)]PF_6$ (2.5×10^{-4} M) at $-90\,^{\circ}C$ in a UV cell (path length: 1 cm). Inset: resonance Raman spectra of frozen solutions of $[Cu_2^{III}([D_4]\mathbf{L^H})_2(\mu\text{-}^{16}O)_2](PF_6)_2$ (——) and $[Cu_2^{III}([D_4]\mathbf{L^H})_2(\mu\text{-}^{18}O)_2](PF_6)_2$ (----) in [D$_6$]acetone; "s" denotes a solvent absorption band.

copper(III) complexes.[5, 15] These spectral features firmly demonstrate that the oxygenated intermediate formed in the present system has a bis(μ-oxo)dicopper(III) core. The rate of formation of the bis(μ-oxo)dicopper(III) complex is second order with respect to the concentration of the starting Cu^{I} complex ($\Delta H^{\neq}=25.3\pm1.1$ kJ mol^{-1} and $\Delta S^{\neq}=-22.8\pm6.0$ J K^{-1} mol^{-1}), which suggests that the bimolecular reaction between an initially formed monomeric superoxocopper(II) complex, $[Cu^{II}(\mathbf{L^X})O_2{}^{\bullet-})]^{+}$, and another Cu^{I} starting compound is rate-determining and that the resulting (μ-peroxo)dicopper(II) intermediate, $[Cu_2^{II}(\mathbf{L^X})_2(\mu\text{-}O_2)]^{2+}$, rapidly converts into the bis(μ-oxo)dicopper(III) species.

When the bis(μ-oxo)dicopper(III) intermediate derived from oxygenation of $[Cu^{I}(\mathbf{L^H})(CH_3CN)]PF_6$ in acetone at $-78\,^{\circ}C$ was warmed and allowed to stand at $25\,^{\circ}C$ for 20 h under an atmosphere of O_2, benzylic hydroxylation of the ligand side arm (phenethyl group) occurred in 46% yield (theoretical maximum is 50%). This result parallels that found previously for the reaction of $[Cu^{I}(\mathbf{L'})]PF_6$ ($\mathbf{L'}=N,N$-bis[2-(2-pyridyl)ethyl]-2-phenylethylamine) with O_2, although the intermediacy of a bis(μ-oxo)dicopper(III) species was not detected directly in this case.[7] The mass spectrum of the modified ligand obtained in the reaction of complexes with $\mathbf{L^H}$ using $^{18}O_2$ (96% labeled) clearly showed that the origin of the oxygen atom of the OH group was molecular oxygen (peak height: M^{+}:(M^{+}+2) = 4.2:100]. In addition, the stoichiometric ratio O_2:Cu for the hydroxylation reaction was determined to be 1:2 by manometry.

Kinetic studies of the ligand hydroxylation revealed it to be a first-order process, presumably involving the intramolecular decay of the bis(μ-oxo)dicopper(III) intermediate. The activation parameters were determined to be $\Delta H_H^{\neq}=39.1\pm0.4$ kJ mol^{-1} and $\Delta S_H^{\neq}=-72.6\pm1.9$ J K^{-1} mol^{-1} (Figure 2, ○). An Eyring plot for the ligand hydroxylation reaction for the complexes with $[D_4]\mathbf{L^H}$ yielded $\Delta H_D^{\neq}=52.8\pm0.5$ kJ mol^{-1} and $\Delta S_D^{\neq}=-31.1\pm2.3$ J K^{-1} mol^{-1}; the observed kinetic deuterium isotope effect (KIE) was 35.4 at $-80\,^{\circ}C$. The effects of *p*-substituents on the hydroxylation process were also examined using $\mathbf{L^X}$ (X = OMe, Me, H, Cl, NO_2) and the Hammett plot of

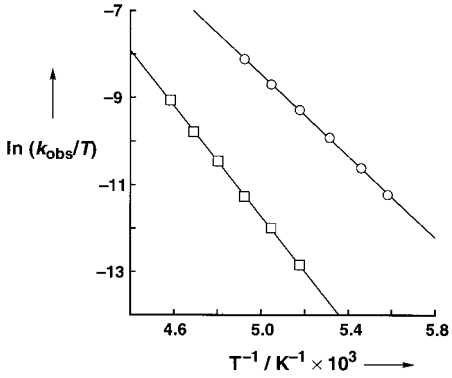
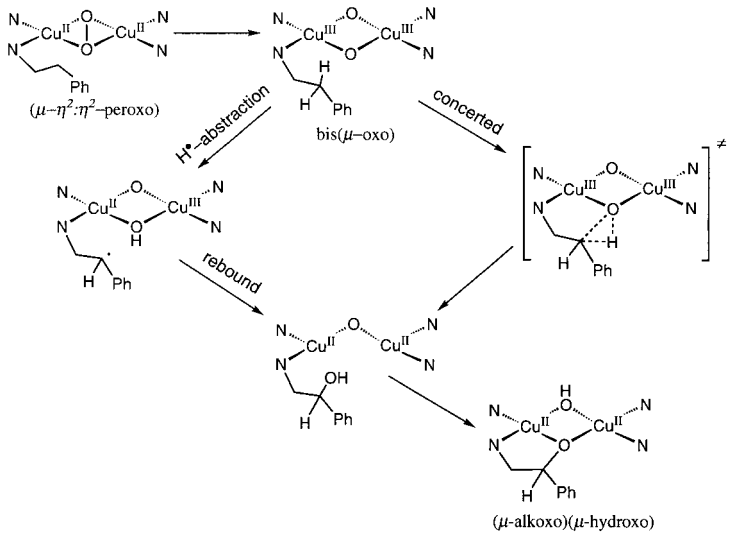


Figure 2. Eyring plots for the ligand hydroxylation of $[Cu_2^{III}(\mathbf{L^H})_2(\mu\text{-}O)_2](PF_6)_2$ (○) and $[Cu_2^{III}([D_4]\mathbf{L^H})_2(\mu\text{-}O)_2](PF_6)_2$ (□) in acetone.

the first-order rate constant k_{obs} versus σ^{+} [16] gave $\rho=-1.48$ ($R=0.99$).[17] Overall, the activation parameters, KIE, and ρ value for the ligand hydroxylation are similar to those measured previously for the oxidative N-dealkylation reaction of $[(L^{iPr_3}Cu)_2(\mu\text{-}O)_2](ClO_4)_2$ (L^{iPr_3} = 1,4,7-triisopropyl-1,4,7-triazacyclononane); ($\Delta H_H^{\neq}=55.2\pm2.1$ kJ mol^{-1}, $\Delta S_H^{\neq}=-59\pm8$ J K^{-1} mol^{-1}, $\Delta H_D^{\neq}=62.7\pm2.1$ kJ mol^{-1}, $\Delta S_D^{\neq}=-50\pm8$ J K^{-1} mol^{-1}; KIE = 26 at $-40\,^{\circ}C$ in THF; $\rho=-0.8$).[11] Thus, we propose a mechanism for the benzylic hydroxylation that is similar to that suggested for the N-dealkylation reaction, involving either abstraction of a hydrogen atom by core **B** followed by rebinding of a hydroxyl group or a concerted variant (Scheme 1).[11]



Scheme 1. Mechanism for the hydroxylation of the ligand.

In conclusion, by using the supporting ligand $\mathbf{L^X}$ we have observed the clean generation of core **B** followed by aliphatic hydroxylation at the ligand benzylic position through a rate-controlling activation of a C–H bond by the bis(μ-oxo)dicopper unit. A similar hydroxylation occurs in the system supported by **L′**,[7] but the kinetic data show that the intramolecular peroxo → bis(μ-oxo) isomerization instead of C–H bond breaking is rate-controlling. Thus, a simple change in the denticity of the supporting ligand results in an important shift

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in the relative rates of O–O and C–H bond scission in these dicopper compounds. These results suggest the possible importance of similar ligand effects on related pathways traversed during aliphatic hydroxylations by copper-containing enzymes and other synthetic systems.

Experimental Section

Product analysis and stoichiometry: $[Cu^{I}(\mathbf{L^{H}})(CH_3CN)]PF_6$ (0.3 mmol) was dissolved in deaerated acetone (10 mL) under anaerobic conditions, and the solution was cooled down to $-78\,^{\circ}C$ using a dry ice/acetone bath. The solution was then exposed to O_2 gas for 1 h at this temperature, and the mixture was further stirred for 20 h at 25 °C. An ordinary work-up treatment of the reaction mixture with aqueous NH_4OH followed by extraction with CH_2Cl_2 and evaporation gave a mixture of organic products (the ^1H NMR yield was determined at this point as described below), from which the hydroxylated ligand *N*-ethyl-*N*-[2-(2-pyridyl)ethyl]-2-hydroxy-2-phenylethylamine ($\mathbf{L^{H}_{OH}}$) was isolated by flash column chromatography (SiO_2, $CHCl_3/CH_3OH$, 100/15). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.99$ (t, $^3J(H,H) = 7.2$ Hz, 3H; CH_3), 2.48–2.79 (m, 4H; CH_2), 2.88–3.10 (m, 4H; CH_2), 4.62 (dd, $^3J(H,H) = 3.4$, 10.2 Hz, 1H; CH), 7.13 (ddd, $^3J(H,H) = 4.8$, 7.8 Hz, $^4J(H,H) = 0.8$ Hz, 1H; Py-H_5), 7.18 (d, $^3J(H,H) = 7.8$ Hz, 1H; Py-H_3), 7.26 (dd, $^4J(H,H) = 1.6$, $^3J(H,H) = 4.8$ Hz, 1H; *p*-Ph), 7.31–7.38 (m, 4H; *o*- and *m*-Ph), 7.61 (dt, $^4J(H,H) = 1.6$, $^3J(H,H) = 7.8$ Hz, 1H; py-H4), 8.55 (ddd, $^5J(H,H) = 0.8$, $^4J(H,H) = 1.6$, $^3J(H,H) = 4.8$ Hz, 1H; py-H6); FT-IR (neat): $\tilde{\nu} = 3340$ (OH), 1060 cm^{-1} (C–O); MS (positive ion CI): m/z: 271 $[M^+ + 1]$.

The yield of the hydroxylated product $\mathbf{L^{H}_{OH}}$ was determined as 46% by using an integral ratio in the ^1H NMR spectrum between the methine proton (C*H*OH) at $\delta = 4.62$ of $\mathbf{L^{H}_{OH}}$ and the pyridine protons at the 6-position (Py-H_6, $\delta = 8.55$) from both $\mathbf{L^{H}}$ and $\mathbf{L^{H}_{OH}}$ (Py-H_6 signals of $\mathbf{L^{H}}$ and $\mathbf{L^{H}_{OH}}$ are overlapped); (C*H*OH):(Py-H_6) = 0.46:2.00.

The O_2-uptake measurement was carried out on the reaction of $[Cu^{I}(\mathbf{L^{H}})(CH_3CN)]PF_6$ (148.2 mg, 0.294 mmol) in acetone (10 mL) at $-78\,^{\circ}C$. The volume of O_2 consumed during the oxygenation reaction was determined to be 3.51 mL from the difference in the O_2 consumption between the ligand hydroxylation reaction and the blank solution without the reactants under exactly the same conditions using a manometer designed for the small-scale reaction. Thus, the stoichiometry of O_2:Cu was calculated to be 1:2.03.

Kinetic measurements: The reactions of the copper(I) complexes and O_2 were performed in a 1 cm path length UV/Vis cell that was held in a thermostated cell holder designed for low temperature experiments (Unisoku, fixed within $\pm 0.5\,^{\circ}C$). After the deaerated solution of the copper(I) complex (2.5×10^{-4} M) in the cell had been kept at the desired temperature for several minutes, dry dioxygen gas (25 mL) was bubbled through over 5 s by injection from a 25 mL syringe. The formation of the bis(μ-oxo)dicopper(III) intermediate and the subsequent ligand hydroxylation process were followed by monitoring the absorption band at 402 nm.

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[13] Analytical data for $[Cu^{I}(\mathbf{L^{H}})(CH_3CN)]PF_6$: ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 1.21$ (t, $^3J(H,H) = 7.2$ Hz, 3H; CH_2CH_3), 2.17 (s, 3H; coordinated CH_3CN), 2.82–3.17 (m, 10H; CH_2), 7.20 (d, $^3J(H,H) = 7.4$ Hz, 1H; Py-H3), 7.32–7.41 (m, 6H; Ph and py-H5), 7.84 (dt, $^4J(H,H) = 2.0$, $^3J(H,H) = 7.4$ Hz, 1H; py-H4), 8.13 (dd, $^3J(H,H) = 5.2$, $^4J(H,H) = 2.0$ Hz, 1H; py-H6); FT-IR (KBr): $\tilde{\nu} = 837$ cm^{-1} (PF_6^-); Elemental analysis calcd for $[Cu^{I}(\mathbf{L^{H}})(CH_3CN)]PF_6 \cdot 0.5\,H_2O$ ($C_{19}H_{26}N_3O_{0.5}CuPF_6$): C 44.49, H 5.11, N 8.19; found: C 44.46, H 4.91, N 8.08.

[14] The molar absorption coefficient (ε) at 402 nm was determined by using the deuterated ligand $[D_4]\mathbf{L^{H}}$ because the subsequent ligand hydroxylation reaction was much slower than for the case of ligand $\mathbf{L^{H}}$ itself, which enabled the value to be determined accurately.

[15] The isotope-sensitive features in Figure 1 are attributable to Cu_2O_2 core vibrations, and show a striking resemblance to those in a bis(μ-oxo)dicopper complex of another bidentate pyridine/amine ligand.[9] The presence of multiple Cu_2O_2 core vibrations is a result of the lowered core symmetry in these complexes: P. L. Holland, C. J. Cramer, K. R. Rodgers, E. C. Wilkinson, S. Mahapatra, S. Itoh, M. Taki, S. Fukuzumi, L. Que, Jr., W. B. Tolman, unpublished results.

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[17] The *p*-substitution ($\mathbf{L^{X}}$) and the ligand deuteration ($[D_4]\mathbf{L^{H}}$) hardly affect the absorption maximum λ_{max} of the intermediates (402 nm).

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