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Solvent Effects on the Conversion of Dicopper(II) μ-η^2:η^2-Peroxo to Bis-μ-oxo Dicopper(III) Complexes: Direct Probing of the Solvent Interaction

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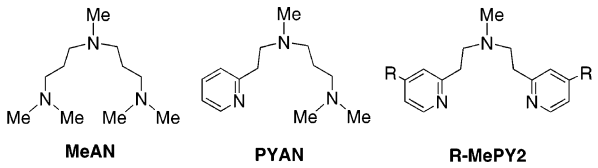
A new tridentate ligand, PYAN, is employed to investigate solvent influences for dioxygen reactivity with [Cu(PYAN)(MeCN)]B(C_6F_5)$_4$ (**1**). Stopped-flow kinetic studies confirm that the adducts [{Cu^{II}(PYAN)}$_2$(O_2)][B(C_6F_5)$_4$]$_2$ (**2**^{Peroxo}) and [{Cu^{III}(PYAN)}$_2$(O)$_2$][B(C_6F_5)$_4$]$_2$ (**2**^{Oxo}) are in rapid equilibrium. Thermodynamic parameters for the equilibrium between **2**^{Peroxo} and **2**^{Oxo} are as follows: THF, $\Delta H^\circ \sim -15.7$ kJ/mol, $\Delta S^\circ \sim -83$ J/K·mol; acetone, $\Delta H^\circ \sim -15.8$ kJ/mol, $\Delta S^\circ \sim -76$ J/K·mol. UV–visible absorption and resonance Raman spectroscopic signatures demonstrate that the equilibrium is highly solvent dependent; the mixture is mostly **2**^{Peroxo} in CH_2Cl_2, but there are significantly increasing quantities of **2**^{Oxo} along the series methylene chloride → diethyl ether → acetone → tetrahydrofuran (THF). Copper(II)–N_{eq} stretches (239, 243, 244, and 246 cm^{-1} in CH_2Cl_2, Et_2O, acetone, and THF, respectively) are identified for **2**^{Peroxo}, but they are not seen in **2**^{Oxo}, revealing for the first time direct evidence for solvent coordination in the more open **2**^{Peroxo} structure.

Previous studies on copper−dioxygen reactivity demonstrate that Cu(I) complexes with various tridentate[1] or bidentate[2,3] amine ligands can react with O_2 to form both the μ-η^2:η^2-(side-on)-peroxo dicopper(II) and/or the bis-μ-oxo dicopper(III) cores, and that these species can rapidly interconvert depending on reaction conditions.[4−8] In continuing efforts to understand the factors that bias this equilibrium, we use UV−visible absorption and resonance Raman spectroscopic studies, as well as reaction kinetics analyses, to demonstrate the importance of solvent, and in particular to detect copper−solvent molecule binding.

Recently we reported on new Cu(I) complexes with ligands MeAN (see diagram) and AN,[9] which, differing by only one methyl group in their ligand structure (i.e., −CH_3 vs −H), react with dioxygen in CH_2Cl_2 to form disparate copper−dioxygen adducts, i.e., side-on peroxo or bis-μ-oxo species, respectively.[10] We also investigated the reactivity of a copper(I) complex with the ligand R-MePY2 (see diagram), where



ligand electronics (i.e., −R) strongly influence the side-on peroxo/bis-μ-oxo equilibrium.[11] Here, PYAN, a hybrid of MeAN and MePY2, is examined with respect to the dioxygen reactivity of its Cu(I) complex, [Cu^{I}(PYAN)(MeCN)]B(C_6F_5)$_4$ (**1**), in a variety of solvents.

Complex **1** possesses a tetracoordinate copper(I) center with three N-donors from the PYAN ligand and a fourth

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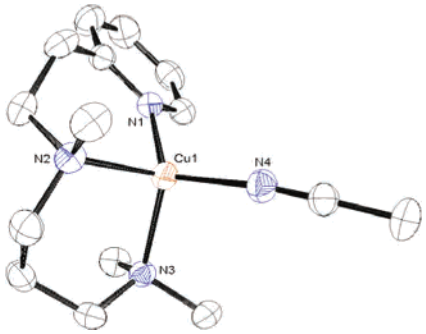

Figure 1. ORTEP diagram of the cationic portion of [Cu(PYAN)(MeCN)]$B(C_6F_5)_4$.

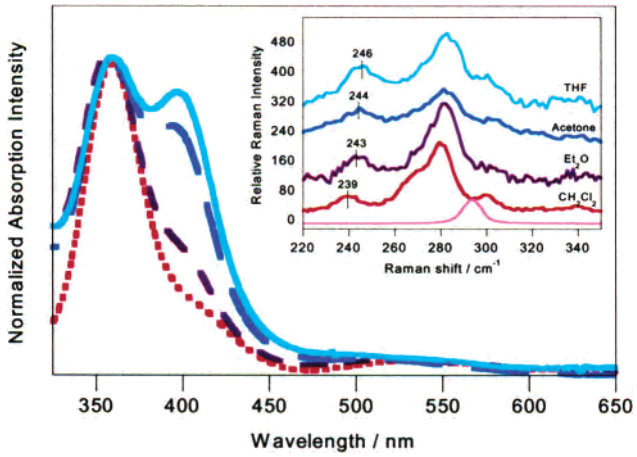

Figure 2. Absorption spectra of $[\{Cu(PYAN)\}_2O_2]^{2+}$ in CH_2Cl_2 (red ···), diethyl ether (purple - - -), acetone (blue — — —), and THF (aqua —). Inset: rR spectra (λ_{ex} = 363.8 nm) of $[\{Cu(PYAN)\}_2{}^{16}O_2]^{2+}$ in CH_2Cl_2, diethyl ether, acetone, and THF [Note: Solvent has been subtracted from the CH_2Cl_2 trace. The scaled CH_2Cl_2 spectrum is shown at bottom for comparison.]

N-donor from acetonitrile (Figure 1).[12] It reacts with O_2 to form varying quantities of side-on peroxo and bis-μ-oxo isomers, $[\{Cu^{II}(PYAN)\}_2(O_2)]^{2+}$ ($\mathbf{2^{Peroxo}}$) and $[\{Cu^{III}(PYAN)\}_2(O)_2]^{2+}$ ($\mathbf{2^{Oxo}}$), respectively: the relative amount of each isomer is highly dependent on solvent (vide infra).[1,7,10,13] As seen by the UV−visible signatures associated with $\mathbf{2^{Peroxo}}$ (360 nm) and $\mathbf{2^{Oxo}}$ (400 nm),[8] **1** reacts with O_2 at −80 °C to form almost all $\mathbf{2^{Peroxo}}$ in CH_2Cl_2. A greater proportion of the isomeric $\mathbf{2^{Oxo}}$ forms in diethyl ether (Et_2O) and acetone, while the highest ratio of $\mathbf{2^{Oxo}}$ to $\mathbf{2^{Peroxo}}$ (∼1:1) forms in tetrahydrofuran (THF) (Figure 2). Resonance Raman (rR) studies confirm the conclusions from the UV−vis spectra:[8,14] excitation into the 360 nm band produces a characteristic side-on peroxo spectrum with ν(Cu···Cu) ∼ 280 cm^{-1} (Figure 2, inset) and ν(O−O) = 714 cm^{-1} ($^{16,18}\Delta$ = −36),[12,15] while 400 nm excitation produces a characteristic dicopper(III) bis-μ-oxo spectrum, ν(Cu−O) = 585 cm^{-1} ($^{16,18}\Delta$ = −25 cm^{-1}).[12] Thus, the growth of the 400 nm absorption feature in the UV−vis spectra of **2** reflects a

Scheme 1. Kinetic Model for the Oxygenation of **1**

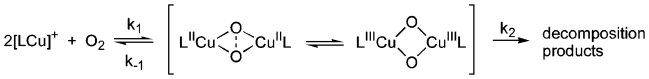

Table 1. Rate Constants (203 K) and Activation Parameters for the Processes in Scheme 1 in Various Solvents

parameter	acetone	THF	CH_2Cl_2
k_1 (M^{-2} s^{-1})	(1.50 ± 0.02) × 10^5	(4.2 ± 0.1) × 10^3	(2.10 ± 0.03) × 10^3
$\Delta H_1^{\ddagger}$ (kJ/mol)	−13.8 ± 0.2	1.6 ± 0.3	−5.1 ± 0.3
$\Delta S_1^{\ddagger}$ (J/K·mol)	−211 ± 1	−165 ± 1	−203 ± 1
k_{-1} (s^{-1})	(5.0 ± 0.8) × 10^{-5}	(9.7 ± 1.0) × 10^{-5}	(1.1 ± 0.1) × 10^{-4}
$\Delta H_{-1}^{\ddagger}$ (kJ/mol)	66 ± 1	60.5 ± 0.9	55 ± 1
$\Delta S_{-1}^{\ddagger}$ (J/K·mol)	−1 ± 6	−21 ± 4	−48 ± 5
k_2 (s^{-1})	(7.7 ± 0.1) × 10^{-4}	(2.5 ± 0.1) × 10^{-4}	*a*
$\Delta H_2^{\ddagger}$ (kJ/mol)	39.9 ± 0.3	46.6 ± 0.5	86 ± 6
$\Delta S_2^{\ddagger}$ (J/K·mol)	−105 ± 1	−81 ± 2	69 ± 25
K_1 (M^{-2})[b]	3.0 × 10^9	4.3 × 10^7	1.8 × 10^7
$\Delta H_1°$ (kJ/mol)	−79 ± 1	−58.9 ± 0.9	−60 ± 1
$\Delta S_1°$ (J/K·mol)	−209 ± 6	−144 ± 4	−155 ± 5

[a] k_2 value uncertain due to photochemistry. [b] Calculated as k_1/k_{-1}.

significant shift in the equilibrium from $\mathbf{2^{Peroxo}}$ toward $\mathbf{2^{Oxo}}$ along the solvent series CH_2Cl_2 → Et_2O → acetone → THF.

To provide further insights, the stopped-flow kinetics of oxygenation of **1** were analyzed in CH_2Cl_2, acetone, and THF. The observed behavior conforms to the kinetic model shown in Scheme 1, confirming that the two Cu_2O_2 species are in rapid equilibrium as also seen in other systems.[4,7,13] In all solvents, oxygenation occurs with negative or very weakly positive activation enthalpies, indicative of an initial formation of the unstable superoxo complex, $[Cu^{II}(PYAN)(O_2^-)]^+$ in a rapid left-lying preequilibrium, as previously observed in analogous copper complexes of tridentate amine ligand systems.[10] The enthalpic stability for the oxygenation reaction is considerably greater in acetone versus THF or CH_2Cl_2 (Table 1). Also, the rate constant for the oxygenation of **1** in acetone is two orders of magnitude greater than the k_1 in THF and in CH_2Cl_2 (Table 1). A clear solvent effect is demonstrated, yet the reasons for the difference in rates are not understood at this time. Similar enhanced oxidation rates in acetone occur with the ligands AN[9,10,16] and H-MePY2.[17,18]

In THF and acetone, over the temperature range of 173 K to 263 K, the spectral changes reflecting the variation in relative amounts of $\mathbf{2^{Peroxo}}$ and $\mathbf{2^{Oxo}}$ allow for estimations of the thermodynamic parameters for the $\mathbf{2^{Peroxo}} \leftrightarrows \mathbf{2^{Oxo}}$ equilibrium. The parameters are identical within experimental uncertainty for the two solvents: THF, $\Delta H°$ ∼ −15.7 ± 0.4 kJ/mol, $\Delta S°$ ∼ −83 ± 2 J/K·mol; acetone, $\Delta H°$ ∼ −15.8 ± 1.2 kJ/mol, $\Delta S°$ ∼ −76 ± 6 J/K·mol.[12] These findings are in good agreement with literature values for related systems ($\Delta H°$ = −3.8 kJ/mol·K, $\Delta S°$ = −25 J/mol·K;[7] $\Delta H°$ ∼ −2.5 kJ/mol·K, $\Delta S°$ ∼ −8.4 J/mol·K[13]), reconfirming the very small barrier for peroxo/bis-μ-oxo isomerization.[19] The bis-μ-oxo dicopper(III) species is enthalpically but not

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entropically favored relative to the side-on peroxo dicopper(II) isomer. The $Cu_2(O)_2$ enthalpic stabilization is most likely due to the stronger (and therefore more rigid) Cu^{III}−ligand bonds.

Further key insights come from rR spectroscopic data. Analysis of the low frequency region suggests that solvent directly interacts with the Cu_2-O_2 core of $\mathbf{2^{Peroxo}}$ but not $\mathbf{2^{Oxo}}$. Previous rR spectroscopic studies with proteins and model compounds support the assignment of the peaks attributed to the side-on peroxo dicopper(II) core: the intense peak at ~300 cm^{-1} represents the Cu···Cu stretching mode, and the weaker satellites are N-equatorial (N_{eq}) vibrations.[20,21] The spectrum of $\mathbf{2^{Peroxo}}$ exhibits vibrational features in CH_2Cl_2 at 239, 278, and 297 cm^{-1}, where the most intense feature at 278 cm^{-1} corresponds to the ν(Cu···Cu) mode. The satellite peak observed at 239 cm^{-1} in CH_2Cl_2 shifts to 243 cm^{-1} in Et_2O, to 244 cm^{-1} in acetone, and to 246 cm^{-1} in THF (Figure 2, inset), significant shifts of 4−7 cm^{-1} (out of ~240 cm^{-1}). This pattern correlates with the solvent dependent shift of the equilibrium constant toward the bis-μ-oxo species $\mathbf{2^{Oxo}}$, yet does not follow the trend in solvent dielectric constants, as previously reported.[6,7] In contrast, the rR feature at 587 cm^{-1} associated with $\mathbf{2^{Oxo}}$ does *not* show a significant shift ($\Delta = 2$ cm^{-1}) upon a change in solvent from CH_2Cl_2 to THF.[12] Thus, despite the fact that the bis-μ-oxo feature is at much higher energy (590 cm^{-1} vs 240 cm^{-1}), its shift is negligible compared to the proportionally much larger 7 cm^{-1} shift of $\mathbf{2^{Peroxo}}$ at ~ 240 cm^{-1}. These effects have been reproducibly observed in other systems.[22]

The UV−vis data imply that using solvents with greater coordinating ability shifts the equilibrium from $\mathbf{2^{Peroxo}}$ to $\mathbf{2^{Oxo}}$. Following the same solvent trend, rR spectra show an increase in energy of the Cu−N_{eq} and Cu···Cu vibrations of the side-on peroxo complex, suggesting that the N_{eq} donors have moved more into the CuN_2O_2 plane. The resulting greater in-plane orbital overlap would lead to strengthened Cu−N_{eq} and Cu_2O_2 bonds. The negligible solvent dependent change in the rR spectra of $\mathbf{2^{Oxo}}$ indicates that this species is less susceptible to such solvent effects (e.g., axial coordination), which seems a reasonable presumption for a tight Cu(III)−N_2O_2 core. However, overall thermodynamic considerations which favor $\mathbf{2^{Oxo}}$ require that these coordinating solvents effect an overall greater stabilization of the $\mathbf{2^{Oxo}}$ isomeric form; the nature of this interaction is not clear at this time.

In conclusion, the combined data demonstrate that solvent interaction and/or binding can be probed and plays a key role in the dynamic equilibrium between the side-on peroxo $Cu^{II}_2-(O_2)$ and bis-μ-oxo $Cu^{III}_2-(O)_2$ isomeric forms. We plan continued efforts to sort out the issues governing the formation, interconversion, and substrate reactivity tendencies of these copper−dioxygen adducts.

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Supporting Information Available: Synthetic details, selected bond lengths and angles, kinetics (UV−vis traces and Eyring plots), resonance Raman, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Besides PYAN, this effect has been seen in the MeAN system (ref 10; see also Figure S4 in Supporting Information). Large shifts for the side-on peroxo but not bis-μ-oxo complexes have also been seen in other peroxo/oxo systems (Mahadevan, V.; Henson, M. J.; Stack, T. D. P.; Solomon, E. I. Unpublished results).