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Contrasting Copper−Dioxygen Chemistry Arising from Alike Tridentate Alkyltriamine Copper(I) Complexes

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Copper−dioxygen interactions are ubiquitous and essential in biological and industrial processes. Multidentate ligands with N-donor-atoms are known to impart O_2-reactivity to the resulting copper(I) complexes.[1−5] Spectroscopic and structural studies show that a diversity of Cu_n-O_2 binding modes exists.[1−5] Besides the μ-1,2 (end-on Cu···Cu ≈ 4.3 Å) and the μ-η^2:η^2 (side-on Cu···Cu ≈ 3.6 Å) (as seen in the O_2-carrier protein hemocyanins)[6] dicopper(II)−peroxo complexes, Cu_n/O_2 reactions can also lead to Cu(III)−bis-μ-oxo species ($Cu_n-(O)_2$, $n = 2$ or 3[7]). In fact, the research groups of Tolman[8,9] and Stack[10,11] have demonstrated that using different tridentate or bidentate alkylamine ligands, and depending on conditions (i.e., solvent, counteranion),[11,12] a given Cu(I) compound can react with O_2 to form both the μ-η^2:η^2-peroxo− or the bis-μ-oxo−dicopper(III) cores (Cu···Cu ≈ 2.7 Å) and that these species may be in rapid equilibrium.[8,9,11,13]

Here, we report on new chemistry utilizing copper(I) complexes of the tridentate ligands AN and MeAN (AN = 3,3′-iminobis(*N*,*N*-dimethylpropylamine; MeAN = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldipropylenetriamine).[14] These alkylamine chelates were chosen for study because of their close analogy to our previously studied derivatives of bis[2-(2-pyridyl)ethyl]amine (PY2),[15−17] containing six-membered chelate rings.[2,18,19] While AN and MeAN differ by only one methyl group in their ligand structure, the formation, O_2-structure-type and reactivity of O_2-adducts of $[Cu^I(MeAN)]^+$ (**1**) and $[Cu^I(AN)]^+$ (**2**) differ drastically, offering new results and insights.

$[Cu^I(MeAN)]B(C_6F_5)_4$ (**1-B(C₆F₅)₄**) and $[Cu^I(AN)](B(C_6F_5)_4)$ (**2-B(C₆F₅)₄**) were synthesized by reaction of 1 equiv of $[Cu^I(MeCN)_4]B(C_6F_5)_4$[20] with the corresponding ligands.[14] The complexes possess tricoordinate copper(I) centers, even when isolated from acetonitrile as solvent; their PY2 analogues tenaciously bind RCN donors as fourth ligands.[15,17,21,22] Complexes **1** and **2** possess nearly identical structures (Figure 1),[14] adopting distorted trigonal planar configurations. The "outer" ∠ N(1)−Cu(1)−N(3) angles are 151.0(2)° and 152.1(2)° for **1** and **2**, respectively, close to that seen for other tricoordinate structures with the PY2 moiety.[23−25] No significant differences occur in Cu−N bond lengths.[14]

Although **1** and **2** differ by a single $-CH_3$ versus −H substituent, their reactivities toward dioxygen differ drastically in CH_2Cl_2, Scheme 1. $[Cu^I(MeAN)]^+$ (**1**) reacts at 193 K giving essentially only the μ-η^2:η^2 (side-on) complex $[\{Cu^{II}(MeAN)\}_2(O_2)]^{2+}$ (**3**). By contrast, only the μ-oxo species $[\{Cu^{III}(AN)\}_2(O)_2]^{2+}$ ($\mathbf{4^{Oxo}}$) is obtained with $[Cu^I(AN)]^+$ (**2**).[26]

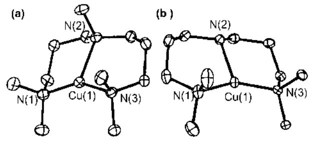


Figure 1. ORTEP diagrams of the cationic portions of complexes $[Cu^I(MeAN)]B(C_6F_5)_4$ (**1-B(C₆F₅)₄**) and $[Cu^I(AN)]B(C_6F_5)_4$ (**2-B(C₆F₅)₄**).[14]

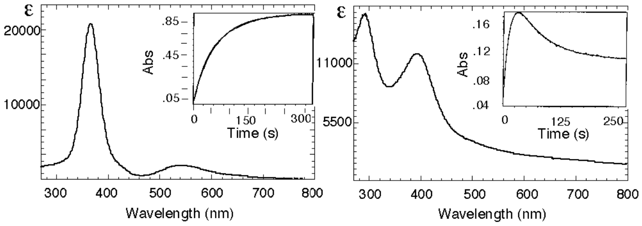
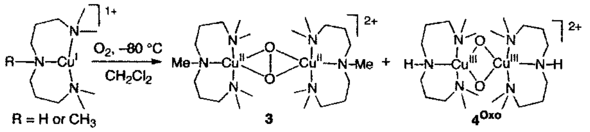


Figure 2. UV−vis spectra (193 K) in CH_2Cl_2 of $[\{Cu^{II}(MeAN)\}_2(O_2)]^{2+}$ (**3**) (left) and $[\{Cu^{III}(AN)\}_2(O)_2]^{2+}$ ($\mathbf{4^{Oxo}}$) (right). Insets: kinetic traces (179 K) monitored at 366 nm for **3** and 386 nm for $\mathbf{4^{Oxo}}$ (ϵ, M^{-1} cm^{-1}).

Scheme 1



$[\{Cu^{II}(MeAN)\}_2(O_2)]^{2+}$ (**3**) formed in CH_2Cl_2 (Scheme 1) is formulated as a side-on μ-η^2:η^2-peroxo complex based on its typical[11,12] absorption bands at 360 nm (ϵ 22 000 M^{-1} cm^{-1}) and 540 nm (ϵ 2500 M^{-1} cm^{-1}), Figure 2. Confirmation comes from resonance Raman measurements, which exhibited a characteristic[13,27] but very low[4] $\nu_{O-O} = 721$ cm^{-1} ($^{16}O_2$ 683 cm^{-1} with $^{18}O_2$),[28] plus a diagnostic[29] ν_{Cu-Cu} band at 268 cm^{-1} which corresponds to a vibrational mode involving primarily Cu···Cu motion.[14] The bis-μ-oxo-dicopper(II) core in $[\{Cu^{III}(AN)\}_2(O)_2]^{2+}$ ($\mathbf{4^{Oxo}}$) is deduced from the UV−vis absorptions at 293 nm (ϵ 15 000 M^{-1} cm^{-1}) and 393 nm[30] (ϵ 12 000 M^{-1} cm^{-1}) (Figure 2) and from its characteristic[13,27] resonance Raman Cu_2O_2 core vibration $\nu_{Cu-O} = 608$ cm^{-1} ($^{16}O_2$ 580 cm^{-1} with $^{18}O_2$). Both $[Cu^I(MeAN)]^+$ (**1**) and $[Cu^I(AN)]^+$ (**2**) appear to give only these single products in CH_2Cl_2.[26,31,32]

Additional insights have been obtained from stopped-flow kinetics measurements (CH_2Cl_2, 350−700 nm monitoring, −94 to 20 °C). $[Cu^I(MeAN)]^+$ (**1**) reacts reversibly with O_2 (Figure 2 inset) forming $[\{Cu^{II}(MeAN)\}_2(O_2)]^{2+}$ (**3**) with $\Delta H^\ddagger = -27 \pm 3$ kJ/mol, and $\Delta S^\ddagger = -335 \pm 16$ J mol^{-1} K^{-1} ($k_{on} = (6.9 \pm 0.7) \times 10^2$ M^{-2} s^{-1}, 183 K). No intermediates were observed, but the negative activation enthalpy and extremely negative activation entropy presuppose the formation of an unstable superoxo complex $[Cu^{II}(MeAN(O_2^-)]^+$ in a rapid left-lying preequilibrium. Thermo-

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dynamic parameters derived from the reversible kinetics (overall forward and back reactions) are $\Delta H° = -28 \pm 2$ kJ/mol, $\Delta S° = -61 \pm 12$ J mol^{-1} K^{-1} ($K = (7.6 \pm 0.6) \times 10^4$ M^{-2}, 183 K); nearly all other Cu_2O_2 peroxo complexes measured exhibit considerably more negative (favorable) $\Delta H°$ values.[15,33] Compared to $[(MePY2)Cu^I]^+$ reaction with O_2 (in acetone solvent, where the adduct $[((MePY2)Cu)_2(O_2)]^{2+}$ forms),[17,31] the **1**/O_2 reaction is slower and the peroxo product **3** is somewhat less stable. By contrast, in the reaction of $[Cu^I(AN)]^+$ (**2**) with O_2, the bis-μ-oxo product $[\{Cu^{III}(AN)\}_2(O)_2]^{2+}$ (**4^{Oxo}**) forms much faster than does **3** (Figure 2), $\Delta H^{\ddagger} = -9.9 \pm 0.6$ kJ/mol (again implicating a steady state intermediate forms in a preequilibrium), $\Delta S^{\ddagger} = -210 \pm 3$ J mol^{-1} K^{-1}, and $k_{on} = (2.7 \pm 0.1) \times 10^4$ M^{-2} s^{-1}, 183 K. The thermodynamic parameters obtained are distinctive; a *relatively* unfavorable reaction enthalpy (as for formation of **3**), $\Delta H° = -24 \pm 1$ kJ/mol, is accompanied by peculiarly favorable (compared to all other systems)[15,33] reaction entropy $\Delta S° = -14 \pm 6$ J mol^{-1} K^{-1} ($K = (1.02 \pm 0.07) \times 10^6$ M^{-2}, 183 K). While **3** is quite stable at reduced temperatures (i.e., hours, at 193 K), **4^{Oxo}** decomposes relatively quickly (cf., Figure 2, right), $\Delta H° = 35 \pm 2$ kJ/mol, $\Delta S° = -95 \pm 11$ J mol^{-1} K^{-1} $k_{decomp} = (3.0 \pm 0.2) \times 10^{-1}$ s^{-1} at 223 K.

Other remarkable differences are in the solvent dependencies of formation of O_2-adducts of **1** and **2**. The side-on peroxo $[\{Cu^{II}(MeAN)\}_2(O_2)]^{2+}$ (**3**) is the predominant product of O_2 reaction with **1** in CH_2Cl_2, acetone, tetrahydrofuran (THF) and diethyl ether solvents, based on UV−vis or resonance Raman data.[34] $[\{Cu^{III}(AN)\}_2(O)_2]^{2+}$ (**4^{Oxo}**) is formed exclusively from **2**/O_2 reaction in CH_2Cl_2. However, both **4^{Oxo}** and a μ-η^2:η^2 (side-on)-peroxo complex $[\{Cu^{II}(AN)\}_2(O_2)]^{2+}$ (**4^{Peroxo}**) form in acetone $\{\nu_{Cu-Cu} = 271$ cm^{-1}; $\nu_{Cu-O} = 604$ cm^{-1}; $\Delta(^{18}O) = 26$ cm$^{-1}\}$ and THF $\{\nu_{Cu-Cu} = 271$ cm$^{-1}\}$, in a roughly 1:1 proportion (UV−vis criterion).[14] Yet, in diethyl ether, 80−90% (UV−vis criterion) **4^{Peroxo}** forms. Thus, the AN ligand can support either peroxo−$Cu_2(O_2)$ or bis-μ-oxo−$Cu_2(O)_2$ in a strongly solvent dependent manner. It is notable that the bis-μ-oxo versus peroxo preference (THF vs CH_2Cl_2) for the AN ligand complex is opposite to the results seen by the groups of Tolman (with triaza macrocyclic ligands)[12] and Stack (with substituted ethylenediamine ligands).[11] It is important to obtain a further detailed understanding of the factors underlying copper(I)/O_2 chemistry leading to μ-η^2:η^2 (side-on)-peroxo− versus bis-μ-oxo−dicopper(III) species, their relative energetics and their possible differential reactivity toward substrate oxidation.[11,13,35−40] Solvent medium effects (here and previously)[11,12] may be due to environmental (dielectric or solvation) influences or coordination to copper.[41] Sterically demanding ligands have been suggested to favor side-on peroxo−dicopper(II) complex formation,[9,11,12] but a $-CH_3$ versus $-H$ substituent (in MeAN vs AN) is sufficient to shift the course of reaction. H-bonding in complexes of AN could also be important. Further studies are needed.

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Supporting Information Available: Synthetic details, kinetics (UV−vis traces, Eyring and van't Hoff plots), resonance Raman and X-ray crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Results on a system where solvent coordination is clearly indicated will be included in a manuscript currently under preparation.

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