Reversible O₂ Binding to a Dinuclear Copper(I) Complex with Linked Tris(2-pyridylmethyl)amine Units: Kinetic—Thermodynamic Comparisons with Mononuclear Analogues Dong-Heon Lee,[†] Ning Wei,[†] Narasimha N. Murthy,[†] Zoltán Tyeklár,[†]

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Abstract: The kinetics and thermodynamics of reaction of O2 with copper(I) complexes can provide fundamental information relevant to chemical and biological systems. Using diode-array variable-temperature (180-296 K) stopped-flow kinetic methods, we report detailed information on the O₂ reactivity (in EtCN) of dicopper(I) complex $[(D^{1})Cu^{I}_{2}(RCN)_{2}]^{2+}$ (2a) (R = Me or Et) [D¹ = dinucleating ligand with a $-CH_{2}CH_{2}$ - group linking two tris(2pyridylmethyl)amine (TMPA) units at a 5-pyridyl position of each tetradentate moiety]. A comparative study of mononuclear complex $[(TMPAE)Cu(RCN)]^+$ (1a') [TMPAE has a $-C(O)OCH_3$ ester substituent in the 5-position of one pyridyl group of TMPA] has been carried out. The results are compared with data from the previously investigated complex $[(TMPA)Cu(RCN)]^+$ (1a). The syntheses of D¹ and 2a-(ClO₄)₂ are described; an X-ray structure reveals two pentacoordinate Cu(I) ions (Cu···Cu = 11.70 Å), each bound by the N₄-tetradentate and an EtCN molecule. Cyclic voltammetric data for 1a' and 2a are reported. At 193 K in EtCN, 2a reacts with O_2 (Cu/ $O_2 = 2:1$, manometry) to produce an intensely purple colored solution of adduct $[(D^1)Cu_2(O_2)]^{2+}$ (2c), $\lambda_{max} = 540$ nm ($\epsilon = 11\ 100\ M^{-1}$ cm^{-1}). This peroxo-dicopper(II) species reacts with PPh₃, liberating O₂ and producing the isolatable bis-phosphine adduct $[(D^1)Cu_2(PPh_3)_2]^{2+}$. The kinetic investigation provides spectral characterization of transient Cu/O₂ 1:1 adducts generated upon oxygenation of cold solutions of 1a' or 2a. $[(TMPAE)Cu(O_2)]^+$ (1b') forms reversibly ($\lambda_{max} = 415$ nm) with $k_1 = (8.2 \pm 0.4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $K_1 = k_1/k_{-1} = (284 \pm 9) \text{ M}^{-1}$ at 183 K, with $\Delta H_1^{\circ} = (-32 \pm 1) \text{ kJ}$ mol^{-1} , $\Delta S_1^{\circ} = (-127 \pm 3)$ J K⁻¹ mol⁻¹. Two types of Cu(II)-O₂⁻ complexes form in the reaction of 2a: a 2:1 open form (i.e., $[(D^1)Cu_2(O_2)(EtCN)]^{2+}$, 2b) and a bis-O₂ 2:2 open adduct (i.e., $[(D^1)Cu_2(O_2)_2]^{2+}$, 2b'). For the formation of 2b, $k_1 = (1.63 \pm 0.01) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $K_1 = (2.03 \pm 0.04) \times 10^3 \text{ M}^{-1}$ at 183 K. Complexes 2b and 2b' have identical spectroscopic properties ($\lambda_{max} = 416 \text{ nm}$, $\epsilon = 4500 \text{ M}^{-1} \text{ cm}^{-1}$) per Cu–O₂ unit, and their rate constants are statistically related. Intermediates 1b' and 2b further convert into (µ-peroxo)dicopper(II) [(2 Cu):(1 O₂)] complexes. [{(TMPAE)Cu}₂(O₂)]²⁺ (1c') ($\lambda_{max} = 532 \text{ nm}, \epsilon = 9380 \text{ M}^{-1} \text{ cm}^{-1}$) forms in a second-order reaction of 1b' with 1a' with $K_1K_2 = (2.1 \pm 0.4) \times 10^{11} \text{ M}^{-2}$ at 183 K ($\Delta H_{12}^{\circ} = -77 \pm 1 \text{ kJ mol}^{-1}$ and $\Delta S_{12}^{\circ} =$ $-203 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$), while [(D¹)Cu₂(O₂)]²⁺ (**2c**) ($\lambda_{max} = 540 \text{ nm}$, $\epsilon = 11\ 100 \text{ M}^{-1} \text{ cm}^{-1}$) is generated from **2b** in an intramolecular reaction, with $k_2 = (3.51 \pm 0.05) \times 10^1 \text{ s}^{-1}$ and $k_{on} = k_1 k_2 / k_{-1} = (7.1 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (183 K). The overall formation of 2c is faster than for 1c' or $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) because of a more positive entropy of activation ($\Delta S_{on}^{\dagger} = (-139 \pm 3) \text{ J K}^{-1} \text{ mol}^{-1}$ for 2c vs $\Delta S_{on}^{\dagger} = (-201 \pm 5) \text{ J K}^{-1} \text{ mol}^{-1}$ for 1c). However, this significantly enhanced kinetic reactivity (for $2a \rightarrow 2c$) is not reflected by an analogous increase in thermodynamic stability. $[(D^1)Cu_2(O_2)]^{2+}$ (2c) is enthalpically less stable $(\Delta H_{12}^\circ = (-34.8 \pm 0.4) \text{ kJ mol}^{-1})$ than Cu_2O_2 species 1c and 1c' ($\Delta H_{12}^{\circ} = -81$ to -77 kJ mol⁻¹, respectively), which are formed from mononuclear precursors. There is a substantially larger overall formation entropy for 2c [$\Delta S_{12}^{\circ} = (-89.3 \pm 1.5)$ J K⁻¹ mol⁻¹ compared to -220 and -203 J K⁻¹ mol⁻¹ for 1c and 1c', respectively] since Cu₂O₂ formation is an intramolecular, rather than intermolecular, process. Examination of other kinetic parameters and spectral differences provides complementary information that 2c has a strained structure. In fact, 2c is not the ultimate oxidation product: relief of steric constraints occurs at higher temperatures by a slow rearrangement ($\lambda_{max} = 540 \text{ nm} \rightarrow \lambda_{max} = 529 \text{ nm}$) producing $\{Cu_2O_2\}_n$ oligomers containing *intermolecular* $Cu-O_2-Cu$ bonds. A particularly stable trimer species $[\{(D^1)Cu_2(O_2)\}_3]^{6+}$ (2d) was characterized, with $\Delta H_3^{\circ} = (-153 \text{ kJ mol}^{-1})/3 = -51 \text{ kJ mol}^{-1}$ per Cu₂O₂ unit, intermediate between that seen for 2c, 1c, and 1c'. Thus, (peroxo)dicopper(II) complexes formed from mononuclear precursors are the most stable, while secondary rearrangements within intramolecularly formed Cu₂-O₂ complexes with dinucleating ligands can and do occur. Comparisons are made with relevant copper-dioxygen complexes, and the chemical and biological relevance of this chemistry is discussed.

Introduction

Metal-dioxygen (O₂) interactions occur widely in biological systems,¹ at heme (porphyrin-iron) centers,^{2,3} non-heme iron,^{4,5}

and copper enzyme active sites.⁶⁻¹¹ Such processes include O₂ transport, dioxygenation (i.e., incorporation of two atoms

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of O_2 into an organic substrate), hydroxylation by monooxygenases, and dehydrogenation of organics where the reactions are driven by the reduction of O_2 to either hydrogen peroxide or water. As dioxygen in air is the least expensive oxidant or source of oxygen atoms, a detailed understanding of metal- O_2 reactions is important in synthetic or industrial applications.

Our interests have focused on copper-dioxygen reactivity,^{1,9,12} stimulated in large part by the occurrence of copper proteins and enzymes such as hemocyanin (an O₂ carrier in mollusks and arthropods), 6,7,13,14 and enzymes that "activate" O₂, promoting oxygen atom incorporation into biological substrates. The latter include tyrosinase,^{6,7} dopamine β -monooxygenase (DBM),¹⁵⁻¹⁷ and the related peptidyl α -hydroxylating monooxygenase (PHM),^{18,19} as well as a bacterial membrane protein methane monooxygenase.²⁰ The "blue" multicopper oxidases promote substrate (e.g., amine, phenol) one-electron oxidations while reducing O_2 to water.^{21,22} Amine oxidases^{23,24} and galactose oxidase^{25,26} effect amine \rightarrow aldehyde oxidative deaminations and alcohol \rightarrow aldehyde oxidative dehydrogenations, respectively. Respiratory enzymes that transduce energy via coupled proton pumping include the terminal cytochrome cand quinol oxidases.27,28

Interaction of O_2 with active site copper(I) plays a central role in these proteins. This reaction is reversible in the case of hemocyanins, and the adduct formed is a $(\mu - \eta^2: \eta^2 - \text{peroxo})$ -dicopper(II) species.^{13,14} The situation is less clear for other enzymes, but initially formed $Cu_n - O_2$ (n = 1 or 2) adducts

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may undergo further transformation(s), for example, activation (by protonation and/or O-O bond cleavage) in monooxygenases^{6,15} or reduction and protonation in oxidases.^{21,27}

One goal in bioinorganic copper chemistry is to elucidate basic patterns of Cu_n-O₂ binding, structure, associated spectroscopy, and reactivity, in varied copper-ligand environments. Our program and others $^{7-9,29-36}$ involve a model compound approach.¹ Work since 1984 has led to the characterization of a variety of well-defined copper-dioxygen coordination complexes with varying Cu/O₂ stoichiometries (1:1 and 2:1) and different structures, 7,9,12,29,30,37 physical properties, and spectroscopy. Even transient $Cu_n - O_2$ species can be well characterized by employment of suitable polydentate ligands, lowtemperature generation and physicochemical examination, and stopped-flow kinetic investigations.³⁸⁻⁴³ Biomimetic investigations have led to the crystallographic characterization of four copper-dioxygen adducts, two recently described $Cu/O_2 = 1:1$ superoxo-copper(II) species (discussed later)^{29,30} and two Cu/ $O_2 = 2:1$ (peroxo)dicopper(II) compounds. That due to Kitajima and co-workers^{7,44} is ${Cu[HB(3,5-i-Pr_2pz)_3]}_2(O_2)$ $[HB(3,5-i-Pr_2pz)_3 = hydrotris(3,5-diisopropylpyrazolyl)borate$ anion], which has a side-on ligated $(\mu - \eta^2: \eta^2 - \text{peroxo})$ dicopper-(II) structure, with physical properties [i.e., Cu···Cu \sim 3.6 Å, $\nu_{\rm O-O} \sim 750 \ {\rm cm}^{-1}$ (resonance Raman), $\lambda_{\rm max} = \sim 350 \ {\rm nm} \ (\epsilon \sim 10^{-1} \ {\rm cm}^{-1} \ {\rm cm}^{-1}$ 20 000 M^{-1} cm⁻¹)], that closely match those of Limulus polyphemus oxyhemocyanin.^{13,14}

Previously, we had generated and characterized [{(TMPA)-Cu}₂(O₂)]²⁺ (**1c**, Scheme 1), formed from the reversible reaction of O₂ with [(TMPA)Cu(RCN)]⁺ (**1a**); this system utilizes the tripodal tetradentate ligand TMPA (Chart 1), and **1c** possesses a *trans-µ*-1,2-Cu₂O₂²⁺ moiety with Cu···Cu = 4.36 Å.^{45,46} The structural and physical properties of **1c** differ from those seen in {Cu[HB(3,5-*i*-Pr₂pz)₃]}₂(O₂), with $\nu_{O-O} = 831 \text{ cm}^{-1}$ (resonance Raman)⁴⁷ and UV-vis bands at 440 nm ($\epsilon = 2000 \text{ M}^{-1}$

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Chart 1



cm⁻¹), $\lambda_{max} = 525$ nm (11 500), ~600 nm (sh, ~7600), and a d-d band at 1035 nm (180). Strong, multiple absorptions in the near UV and visible spectral region can be assigned as peroxo-to-copper(II) ligand-to-metal charge-transfer (LMCT) bands.¹⁰

We also have reported a complete kinetics/thermodynamics investigation of the reaction of $[(TMPA)Cu(RCN)]^+$ (1a) (R = Me or Et)⁴⁸ with O₂.^{39,40} Initially, a spectroscopically detectable $(\lambda_{max} = 410 \text{ nm}, \epsilon = 4000 \text{ M}^{-1} \text{ cm}^{-1}) \text{ Cu/O}_2 = 1:1 \text{ adduct}$ $[(TMPA)Cu(O_2)]^+$ (1b) [formally a superoxo-copper(II) species] is formed; this reacts rapidly with excess 1a to give $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) (Scheme 1). While 1b and 1c can be studied at low temperatures, the room temperature stability of these (and other Cu₂O₂ complexes)⁹ is rather low because of highly unfavorable reaction entropies; e.g., for 1c, $\Delta S_{12}^{\circ} = -220$ $\pm 11 \text{ J K}^{-1} \text{ mol}^{-1.40}$ We also have seen that the relative stability of Cu-O₂ 1:1 species versus Cu₂-O₂ (i.e., peroxo-bridged) 2:1 complexes greatly depends on the ligand environment and imposed metal coordination, such as when pyridyl groups in TMPA are replaced by quinolyl^{40,49} or imidazolyl⁵⁰ donors.

To better understand critical factors determining copperdioxygen complex structure and O₂-binding kinetic and thermodynamic characteristics, we sought to elaborate the chemistry of the TMPA ligand system. A dinucleating analogue of TMPA, with two tripodal units joined by some organic linker group, was anticipated to stabilize peroxo copper(II) by providing an *intramolecular* version of the second step in Scheme 1. The detailed effects on kinetics/thermodynamics parameters of O_2 reaction with such a dicopper(I) complex would be of interest. Would the same type of Cu/O₂ 1:1 adduct form? Would *intramolecular* binding of O₂ be considerably faster? Would the enthalpy of copper-dioxygen binding be affected? Would or could *intermolecular* chemistry occur?

Thus, the focus of this report is the chemistry of a new dinucleating ligand D1 (Chart 1). Its synthesis and that of a new dicopper(I) complex $[(D^1)Cu_2^I(RCN)_2]^{2+}$ (2a) are given, the X-ray structure of 2a is described, and its Cu(I)2/O2 chemistry is detailed. The ligand D1 was chosen for its ease of synthesis and because hand-held models indicate that it might provide a largely unstrained environment for a peroxodicopper(II) structure close to that observed in [{(TMPA)Cu}2- (O_2)]²⁺ (1c). We also report the Cu(I)/O₂ kinetics and thermodynamics of the mononuclear Cu(I) complex of TMPAE, [(TMPAE)Cu(MeCN)]⁺ (1a') (Chart 1). The X-ray analysis of 1a' 42 has previously given insight into the distorted pentacoordinate structure of this complex and thus, by analogy, of 1a (Scheme 1). The reactions with [(TMPAE)Cu(MeCN)]⁺ (1a') and $[(D^1)Cu_2^{I}(MeCN)_2]^{2+}$ (2a) provide additional data for Cu(I)/O₂ reactivity in this tripodal tetradentate ligand environment, while also giving insight into the relationship between kinetics/thermodynamics and the redox potential of the copper complex as affected by the pyridine substituent, i.e., 5-[-C(O)-OCH₃] or 5-(-CH₂CH₂)-, respectively.

Experimental Section

Methods and Reagents. Reagents and solvents were of commercially available reagent quality unless otherwise stated. Dioxygen was dried over a short column of supported P4O10 (Aquasorb, Mallinkrodt). Propionitrile was first distilled over P4O10, then refluxed, and distilled from CaH2 under argon. Diethyl ether was dried by passing it through a 50-cm column of activated alumina or by direct distillation from sodium benzophenone under Ar. In the dark, CH₂Cl₂ was stirred with concentrated sulfuric acid for several days. After being washed with water and then Na₂CO₃ solution (saturated), it was dried over anhydrous MgSO₄ before a final reflux and distillation from CaH₂. All ligands were made in the air unless otherwise stated. Column chromatography was carried out with alumina; the column size was typically 30 cm \times 3 cm. Preparation and handling of air-sensitive materials were carried out under argon with standard Schlenk techniques. Solvents and solutions were deoxygenated by either repeated vacuum/purge cycles using argon or bubbling of argon (20 min) directly through the solution. Copper(I) solid samples were stored and transferred, and samples for NMR and IR spectra were prepared, in a Vacuum/Atmospheres drybox filled with argon. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

⁽⁴⁸⁾ RCN, MeCN, and EtCN are used somewhat indiscriminately in formulas in this text, since compounds were normally synthesized with MeCN as an additional ligand, but all kinetics experiments were carried out in EtCN.

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Infrared spectra were recorded neat or in Nujol mulls on a Mattson Galaxy 4030 FT-IR spectrometer. NMR spectra were measured in CDCl₃ or CD₃CN on either a Varian (400-MHz) or a Bruker (300-MHz) NMR instrument. All spectra were recorded in 5-mm-o.d. NMR tubes. Chemical shifts were reported as δ values downfield from internal standard Me₄Si. Low-temperature UV-vis spectral studies were carried out with a Hewlett-Packard 8452A diode array spectrometer driven by a Compaq Desk pro 386S computer and software written by OLIS, Inc. The spectrometer was equipped with a variabletemperature dewar and a cuvette assembly as described elsewhere.^{51,52} Gas chromatography was carried out on a Hewlett-Packard 5890 instrument fitted with a 30-m HP-5 (cross-linked 5% phenyl methyl silicone) capillary column. Electron ionization mass spectra were obtained on a double-focusing Vacuum Generator 70-S (VG 70-S) gas chromatography/mass spectrometer. Fast atomic bombardment (FAB) mass spectra were obtained with the VG 70-S instrument.

Synthesis of Ligands: Methyl 6-(Bromomethyl)nicotinate and TMPAE. These compounds were synthesized as previously described.⁴⁵

TMPAOH. Into a two-neck round-bottom flask was added LiAlH₄ (0.6 g, 15.8 mmol) under Ar, followed by 50 mL of Et₂O. At 273 K, TMPAE (5 g, 14.3 mmol) in 150 mL of distilled Et₂O was added dropwise to the LiAlH₄ suspension with stirring. The gray suspension of LiAlH₄ gradually turned yellow. The mixture was slowly warmed to room temperature and stirred overnight (18 h). The yellow suspension changed to brown with time. After the reaction was stopped, 0.6 mL of H₂O was added slowly, followed by 0.6 mL of 10% NaOH and another 0.6 mL of H₂O. When the brown suspension reacted with water, it changed to off-white and the ether layer became yellow. The precipitate was filtered off on a medium frit and washed thoroughly with diethyl ether. The ether layer was collected, combined with the previous filtrate, and dried over MgSO4. The supernatant was separated and concentrated in vacuo to give a brown oil (3.8 g, 83%). This was used without further purification. ¹H NMR (CD₃CN): δ 3.75 (s, 6 H, 3 CH₂), 4.55 (s, 2 H, CH₂OH), 7.145-7.153 (m, 2 H), 7.55-7.61 (m 6 H), 8.42-8.44 (m, 3 H). IR (neat, cm⁻¹): 3250 (vs, br, OH), 2925-2850 (m, CH), 1591 (vs, C=C). Mass spectrum: m/z 321 (M $+ 1)^{+}$.

TMPACI. TMPAOH (1.5 g, 4.70 mmol) in 30 mL of CHCl3 was added with stirring to 10 mL of CHCl₃ containing 2 mL of SOCl₂ at 273 K. The clear yellow TMPAOH solution quickly became cloudy, and some dark oil formed. The reaction mixture was stirred overnight at room temperature. After the reaction was stopped, the solution was concentrated to dryness in vacuo to give a greenish solid. To this was added 50 mL of THF and a 5-10-fold excess of Et₃N, and the mixture was stirred for several hours, resulting in a brown solution with dark brown precipitate. After filtering through a medium frit, the filtrate was collected and concentrated in vacuo to give 2 g of brown oil, which was chromatographed on alumina, eluting with ethyl acetate. The product fraction was collected and concentrated under reduced pressure to afford a white solid (0.8 g, yield 50%) ($R_f = 0.34$, alumina, ethyl acetate). ¹H NMR (CDCl₃): δ 3.87 (s, 4 H, 2 CH₂), 3.89 (s, 2 H, CH₂), 4.57 (s, 2 H, CH₂Cl), 7.13-7.17 (m, 2 H), 7.55-7.69 (m, 6 H), 8.53-8.55 (m, 3 H). IR (Nujol, cm⁻¹): 1589 (vs, C=C), 1566 (s). Mass spectrum: m/z 339 (M + 1)⁺.

Ligand D¹. Under argon, $[Cu(MeCN)_4]PF_6$ (0.8 g, 2.15 mmol) and TMPACl (0.3 g, 0.88 mmol) were added into a 100-mL Schlenk flask. Degassed MeCN (25 mL) was added to the white solid mixture. The solids initially turned to yellow and quickly changed to green; the solution mixture was stirred under argon overnight. The MeCN solvent was evaporated under reduced pressure, giving a green-blue solid. Dichloromethane (50 mL) was added to the solid, and aqueous ammonia (50 mL) was added to strip out the organic ligand. The CH₂Cl₂ layer was collected, the ammonia extraction was repeated, and then the organic layer was washed with water three times. The organic layer was collected and concentrated in vacuo to give a brown oil, which was column chromatographed and eluted with ethyl acetate. The product fraction was collected and the ethyl acetate removed under reduced pressure to afford an off-white solid (50% yield) ($R_f = 0.11$, alumina, ethyl acetate). ¹H NMR (CDCl₃): δ 2.89 (s, 4 H, CH₂CH₂), 3.86 (s, 4 H, 2 CH₂), 3.89 (s, 8 H, 4 CH₂), 7.16-7.12 (m, 4 H), 7.57-7.6 (m, 12 H), 8.35 (d, 2 H), 8.54 (d, 4 H). IR (neat, cm⁻¹): 3061-2926 (m, CH), 1591 (vs, C=C), 1570 (s), 1476 (m), 1433 (s), 1366 (m), 1123 (m). Mass spectrum: m/z 606 (M⁺). FAB mass spectrum: m/z 607 (M + 1)⁺.

Synthesis of Cu(I) Complexes: [(TMPAE)Cu(MeCN)](PF₆) (1a'-PF₆). This was synthesized according to the published procedure.⁴⁵

 $[(D^1)Cu_2(MeCN)_2](ClO_4)_2$ [2a-(ClO_4)_2]. Dioxygen-free MeCN (10 mL) was added to solids D¹ (0.108 g, 0.165 mmol) and [Cu(MeCN)₄]- $ClO_4\ (0.0977\ g,\ 0.299\ mmol)$ in a 100-mL Schlenk flask under argon. Dry diethyl ether (ca. 20 mL) was added to the yellow solution until a slight cloudiness was observed. The solution mixture was filtered through a medium frit. An additional portion of diethyl ether was added to completely precipitate the yellow solid. The supernatant was decanted, and the solid was washed with ether. Drying the yellow solid under vacuum for 2.5 h yielded 0.11 g (73%) of yellow microcrystalline material. Anal. Calcd for Cu₂C₄₂H₄₄N₁₀Cl₂O₈: C, 49.66; H, 4.33; N, 13.79. Found: C, 49.79; H, 4.38; N, 13.66. ¹H NMR (CD₃CN, room temperature): δ 1.97 (s, 6H, 2 MeCN), 2.92 (s, 4 H, CH₂CH₂), 3.5-4.5 (br), 7.5-9 (br). ¹H NMR (CD₃CN, 230 K): δ 1.97 (s, 6 H, 2 MeCN), 2.92 (s, 4 H, CH₂CH₂), 3.84 (s, 12 H, 6 CH₂), 7.32-8.59 (m, 22 H). IR (Nujol, cm⁻¹): 2010 (m, ClO₄overtone), 1599 (s, C=C), 1084 (vs, ClO₄-). X-ray quality yellow crystals were obtained by dissolving 0.1 g of dicopper(I) complex in 5-8 mL of oxygen-free propionitrile and then carefully layering the solution with diethyl ether; crystals of $[(D^1)Cu_2(EtCN)_2](ClO_4)_2$ developed in 2-3 days.

Dioxygen Uptake Manometry. O₂ absorption by **2a**- $(ClO_4)_2$ at 193 K was monitored at constant pressure in a glass buret as previously described.^{51,52} A 25-mL side-arm Schlenk flask containing a propionitrile solution of $[(D^1)Cu_2(MeCN)_2](ClO_4)_2$ (0.457 g, 0.45 mmol) was attached to the manometer system and cooled to 193 K under argon. After evacuation of the flask for 1 h, the stopcock leading to the reaction flask was closed and the buret assembly was equilibrated to 1 atm of O₂ pressure. Then, O₂ was allowed to enter the reaction flask, causing the solution to immediately change to deep purple as the Cu(1) complex reacted. The volume of O₂ taken up was 9.4 mL (after accounting for solvent O₂ uptake), corresponding to a Cu(I)/O₂ ratio of 2.14(±0.05): 1.

Quantitative Determination of O₂ Liberation from [(D¹)Cu₂- (O_2) ²⁺ (2c) and Synthesis of $[(D^1)Cu_2(PPh_3)_2](ClO_4)_2$. After the manometric reaction with O2 was completed, under a dioxygen flow a storage tube containing triphenylphosphine (0.3 g, 1.1 mmol) and filled with O₂ was attached to the Schlenk flask. After the system was equilibrated for 1 h at 193 K, the triphenylphosphine was added to the reaction flask. During 4 h, 7.2 mL of oxygen was liberated from the reaction [76% recovery of the dioxygen originally taken up by dicopper-(I) complex], with formation of a light green solution. The propionitrile solvent was removed by application of a vacuum, giving a light green residue. This green mixture was recrystallized from acetonitrile/ether, resulting in a pale yellow powder of [(D¹)Cu₂(PPh₃)₂](ClO₄)₂ (0.47 g, 73% yield). Elemental anal. of [(D¹)Cu₂(PPh₃)₂](ClO₄)₂. Calcd for Cu₂C₇₄H₆₈N₈P₂Cl₂O₈: C, 60.92; H, 4.67; N, 7.68. Found: C, 60.75; H, 4.44; N, 7.30. ¹H NMR (CD₃CN): δ 2.51 (s, 4 H, CH₂CH₂), 3.98 (s, 4 H, 2 CH₂), 4.04 (s, 8 H, 4 CH₂), 7.17-7.44 (m, 42 H), 7.68-7.70 (m, 4 H), 7.90 (s, 2 H), 8.25 (s, 4 H).

Electrochemistry. Cyclic voltammetry and bulk electrolysis were carried out with a Bioanalytical Systems BAS-100B electrochemistry analyzer connected to a HP-7440A plotter. The cell was a modified standard three-chambered design for handling air-sensitive solutions by use of high-vacuum valves with Viton O-ring seals. Either a platinum disk (BAS MF 2013) or a glassy carbon electrode (GCE, BAS MF 2012) was used as the working electrode. The reference electrode was $Ag^+/AgNO_3$. The measurements were performed at room temperature in DMF solvent containing 0.2 M tetrabutylammonium hexafluorophosphate (TBAHP) and $10^{-3}-10^{-4}$ M copper complex deoxygenated by bubbling it thoroughly with argon.

Stopped-Flow Kinetics Studies. These rapid O₂-binding reactions were followed with a diode-array (359-776 nm, 508 diodes) stopped-flow instrument over the temperature range 180-296 K in dry

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Scheme 2



TMPACI + 2.5 $[Cu^{I}(MeCN)_{4}]PF_{6}$ MeCN/Ar $CH_{2}Cl_{2}/NH_{3}(aq)$

propionitrile and the data subjected to factor analysis and subsequently global analysis using the program KINFIT.⁴⁰ As all of the reaction mechanisms tested were complicated, including steps of second or even third order in concentration of the complex, numerical integration of the appropriate differential equations was used throughout. Fixed spectra of Cu(I) complex and/or dioxygen adducts were used as needed for successful analysis, prominently for separation of forward and reverse rate constants of a given equilibrium and for direct determination of thermodynamic parameters in fast equilibria. Calculation of temperature-dependent analytical concentrations and further details are given in accounts of kinetic/thermodynamic studies of copper(I)complex O2 reactivity.40,41 Besides the reaction steps describing pseudoreversible dioxygen interaction, to be discussed in detail below, normally (and specifically at higher temperatures) slow, ill-defined, irreversible decay was observed. Corresponding rate constants were included into the numerical analysis when needed for fitting purposes, but not analyzed any further.

For [(TMPAE)Cu(MeCN)]⁺ (**1a**'), a total of 64 measurements were used for the final calculations. The concentration of **1a**'-PF₆ was 5.55 × 10⁻⁴ M and [O₂] = 4.4 × 10⁻³ M in the mixed solution. The temperature was varied between 181 and 270 K, and the data collection time ranged from 0.6 to 24 s. Experiments with **1a**'-PF₆ = 1.19 × 10⁻³ M also were carried out to check the reproducibility of the system.

For $[(D^1)Cu^1_2(MeCN)_2]^{2+}$ (2a), eight different Cu(I) concentrations were used to carry out a total of 324 measurements for the final calculations (all series reacted with oxygen-saturated propionitrile solution, $[O_2] = 8.8 \times 10^{-3} \text{ M}$).⁴⁰ The concentrations of mixed Cu(I) solutions were (0.652–6.97) $\times 10^{-4}$ M. The temperature was varied between 180 and 296 K, and the data collection time ranged from 0.5 to 60 s.

Results and Discussion

Ligand Synthesis. The novel dinucleating ligand D¹ was made through a multistep process summarized in Scheme 2 (also see Experimental Section), in fact proceeding via the previously synthesized intermediate TMPAE.⁴⁵ The final step of the synthesis of D¹ used copper(I) as the coordinating ion and reductant for the reductive coupling reaction of the activated halide TMPACl. Low-oxidation-state transition metals effect similar processes involving organic halides; we previously have shown that [(TMPA)Cu^I(RCN)]⁺ (**1a**) can be used to reductively couple a variety of benzylic or other activated organic halides.⁵³ Here, we found that addition of [Cu^I(MeCN)₄]⁺ to TMPACl, containing the tetradentate TMPA moiety, provided coupled product D¹, isolatable in ~50% yield.

Copper(I) Complex Syntheses. [(TMPAE)Cu(MeCN)](PF₆) (**1a'**-PF₆) was synthesized as previously described.⁴⁵ The dicopper(I) complex with D¹, $[(D^1)Cu_2(MeCN)_2]^{2+}$ (**2a**), was generated by adding 1 equiv of the dinucleating ligand to 2 equiv of [Cu(MeCN)_4](ClO_4) under Ar, as described previously for **1a'**.⁴⁵ The synthesis and handling/study of the Cu(I)

$$2[Cu(MeCN)_4](ClO_4) + D^1 \rightarrow [(D^1)Cu_2(MeCN)_2](ClO_4)_2$$

2a-(ClO_4)_2

(53) Jacobson, R. R.; Tyeklár, Z.; Karlin, K. D. Inorg. Chim. Acta 1991, 181, 111-118.



DI

Figure 1. Chem 3-D drawing of $[(D^1)Cu_2(EtCN)_2]^{2+}$ (**2a**). Selected bond distances (Å) and angles (deg): Cu1–N1, 2.423(4); Cu1–N2, 2.097(4); Cu1–N3, 2.111(4); Cu1–N4, 2.071(4); Cu1–N5, 1.984(4); N5–C51_{nitrile}, 1.116(6); Cu1···Cu1, 11.705(2); N1–Cu1–N2, 74.9(2); N1–Cu1–N3, 74.1(2); N1–Cu1–N4, 76.0(1); N1–Cu1–N5, 176.2-(1); N2–Cu1–N3, 116.7(2); N2–Cu1–N4, 109.1(1); N2–Cu1–N5, 104.5(2); N3–Cu1–N4, 114.7(1); N3–Cu1–N5, 103.2(2); N4–Cu1–N5, 107.6(2); Cu1–N5–C51_{nitrile}, 178.3(5).

complexes must be carried out exclusively in organonitrile solvents. In CH_2Cl_2 , **1a**,^{45,53} **1a**', and **2a** all react rapidly with solvent by abstracting a chlorine atom, producing chloro–copper(II) complexes; this behavior also has been observed for copper(I) complexes with tripodal tetradentate ligands containing either quinolyl⁴⁹ or imidazolyl donors.⁵⁰ A bis-triphenylphosphine adduct complex [(D¹)Cu(PPh₃)₂]²⁺ also was generated, by reacting 2 equiv of PPh₃ with [(D¹)Cu₂(O₂)]²⁺ in propionitrile solvent at 193 K (vide infra).

The presence of the organonitrile ligands in $[(TMPAE)Cu-(MeCN)]^+$ (**1a**') and $[(D^1)Cu_2(MeCN)_2]^{2+}$ (**2a**) was confirmed from C, H, N analysis, NMR spectroscopy, and an X-ray crystal structure study of a propionitrile analogue, $[(D^1)Cu_2(EtCN)_2]^{2+}$. Nitrile coordination is observed in many other cases where related tripodal tetradentate ligands contain three pyridine rings.^{45,54} By contrast, copper(I) complexes with tripodal ligands containing quinolyl⁴⁹ or imidazolyl⁵⁰ donor groups do not possess any additional coordinated nitrile ligand, at least in the isolated solids. This difference may be due to the size of the donor group (especially in the quinolyl case) and might also be related to the unexpected lack of O₂ binding to the imidazolyl compounds.

X-ray Structure of $[(D^1)Cu_2(EtCN)_2](ClO_4)_2$ (2a-(ClO₄)₂). Details of the X-ray structure determination and complete tables with positional and thermal parameters, bond distances, and bond angles have been published.⁴² The structure of 2a consists of a centrosymmetric $[(D^1)Cu_2(EtCN)_2]^{2+}$ dication with Cu1··· Cu1' = 11.70 Å (Figure 1). Each Cu(I) center is identically bonded to three pyridyl nitrogen atoms and a nitrogen atom from a propionitrile group. The Cu-N_{py} distances (2.07–2.11 Å) are close to those found in similar mononuclear copper(I) complexes with tripodal tetradentate ligands;⁴⁵ however, they are slightly longer than those observed in tetracoordinated copper(I) complexes (2.0–2.05 Å) with related ligands.^{51,55,56}

⁽⁵⁴⁾ Jacobson, R. R. Ph.D. Thesis, State University of New York at Albany, 1989.

The short $Cu1-N_{RCN}$ distance, 1.98 Å, indicates that the nitrile group is strongly coordinated to the Cu(I) center, as observed in many nitrile-coordinated copper(I) complexes.^{45,52} The Cu-(I) ions in 2a are pentacoordinate, but the geometry may be better described as distorted from tetrahedral, with only a weak interaction between Cu(I) and the "hard" tertiary amine nitrogen N1; Cu1-N1 = 2.423 Å, a value that lies outside the sum of the covalent radii of Cu and N. The N1 nitrogen lone pair clearly points toward the Cu1, as the N1 atom lies 0.341 Å out of the plane (toward copper) formed by the three benzylic carbon atoms. The Cu1 atom is 0.543 Å out of the N2, N3, N4 plane, toward the propionitrile N5 nitrogen atom. Relevant dihedral angles are Cu1-N3-N4/Cu-N2-N5 = 85.99°, Cu1-N3-N5/ $Cu1-N2-N4 = 88.08^{\circ}$, and Cu1-N4-N5/(Cu1-N2-N3 =92.06°. Thus, the copper ligation found in $[(D^1)Cu_2(EtCN)_2]^{2+}$ (2a) is very similar to that observed for the ester-containing complex [(TMPAE)Cu(MeCN)]⁺ (1a')⁴⁵ and in most Cu(II) complexes with this tripodal tetradentate ligand, e.g., [(TMPA)-Cu^{II}Cl]⁺.⁵⁶

¹H NMR Spectrum of [(D¹)Cu₂(MeCN)₂]²⁺ (2a). At room temperature, the ¹H NMR spectrum of D¹ is sharp and the protons of all methylene and pyridine groups are nicely separated. A room-temperature spectrum of 2a is dramatically broadened by comparison (Figure S1, supporting information). The aliphatic protons from the six CH₂ groups directly connected to the N1 and N1' nitrogen atoms and protons of the 6-position of all pyridine rings are not detected. However, aliphatic protons of the -CH₂CH₂- linker between tetradentate L groups, i.e., those further from the Cu(I) centers, are relatively sharp. While a detailed study has not been undertaken for 2a, we have previously shown that [(TMPA)Cu(MeCN)]⁺ (1a) exhibits dynamic behavior in solution,^{54,57} most likely involving coordination exchange where one pyridyl arm is cleaved from the copper ion, as indicated below.



Exactly such a structure is observed in the triphenylphosphine adduct [(TMPA)Cu^I(PPh₃)]⁺, where one pyridyl donor dangles and is uncoordinated.⁴⁵ Thus, broadening of methylene and pyridyl resonances could occur in solution, as the pyridyl groups exchange from "on" to "off" positions. This exchange should be temperature dependent, as observed.⁵⁷ In fact the ¹H NMR spectrum of 2a is sharp when recorded at lower temperature; a 230 K spectrum is shown in Figure S1 (supporting information). Here, all the resonances expected for this diamagnetic dicopper-(I) complex 2a are observed.

Electrochemistry. The half-wave redox potentials for the copper(I) complexes [(TMPA)Cu(MeCN)]⁺ (1a), [(TMPAE)-Cu(MeCN)]⁺ (1a'), and [(D¹)Cu₂(MeCN)₂]²⁺ (2a) were measured by cyclic voltammetry (CV) under argon in dimethylformamide (DMF). The results are provided in Table 1. All copper(I) complexes displayed quasi-reversible behavior with i_{pa}/i_{pc} close to unity. Peak separations were all less than 90 mV at a scan rate of 100 mV/s. The ferrocene/ferrocenium

Table 1. Cyclic Voltammetry Data for Copper(I) Complexes in DMF

complexes	$E_{1/2}({ m mV})^a$	$\Delta E_{\rm p}({\rm mV})$	i _{pa} /i _{pc}
[(TMPA)Cu(MeCN)] ⁺ (1a)	-608	78	0.80
$[(TMPAE)Cu(MeCN)]^+ (1a')$	-550	88	0.85
$[(D^1)Cu_2(MeCN)_2]^{2+}$ (2a)	-619	88	1.00
[(BQPA)Cu] ⁺ ^b	-410 ^b	95	0.96

^a Versus Ag/AgNO₃. ^b Reference 49.



E (VOLT)

Figure 2. Cyclic voltammogram of $[(D^1)Cu^I_2(MeCN)_2]^{2+}$ (2a) in DMF. Scan rate = 100 mV/s.

couple under the same conditions showed $\Delta E_{\rm p} = 89$ mV and $E_{1/2} = 20 \text{ mV vs Ag/AgNO}_3.$

A typical CV scan for $[(D^1)Cu^I_2(MeCN)_2]^{2+}$ (2a) is given in Figure 2. Results from bulk electrolysis correspond to a twoelectron process per dicopper complex, corroborated by comparison with the behavior of mononuclear 1a. These experiments were accompanied by a color change from yellow [i.e., Cu(I) complex] to blue-green [i.e., oxidized Cu(II) species]. The CV of a coulometrically oxidized solution gave the exact complement to that of the original Cu(I) complex solution at the same scan rate. These observations demonstrate an effective reversibility via an overall two-electron-transfer reaction:

$$[(D^{1})Cu_{2}^{II}]^{4+} + 2e^{-} \Rightarrow [(D^{1})Cu_{2}^{I}]^{2+}$$

2a

The electrochemical behavior of $[(D^1)Cu^I_2(MeCN)_2]^{2+}$ (2a) is best explained with a pair of non-interacting copper(I) centers, as also implied by the solid-state structure. The presence of only one apparent redox CV wave has been well-documented in a number of other dicopper(I) and/or dicopper(II) complexes lacking a tight bridging ligand (e.g., halide, RO⁻, etc.), derived from dinucleating ligands with some flexible organic linker between chelating moieties.⁵⁸⁻⁶¹ If $\Delta E_{1/2}$ between two separate processes (i.e., $Cu^{II} - Cu^{II} + e^- \rightarrow Cu^{II} - Cu^I + e^- \rightarrow Cu^I - Cu^I)$ is $<\sim 100-200$ mV, only one wave is generally seen. We have not attempted a more detailed analysis which could be used to estimate the $E_{1/2}$ for the individual redox reactions,⁶² but this has been carried out in a number of cases.^{60,61}

The $E_{1/2}$ value (Table 1) for $[(D^1)Cu_2^I(MeCN)_2]^{2+}$ (2a) is very close to that of the "parent" mononuclear complex [(TMPA)-Cu(MeCN)]⁺ (1a). Many factors are known to influence the

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Table 2. UV-Vis Spectral Data for Copper(I) and Copper Dioxygen Complexes in EtCN: $\lambda_{\text{max}}/\text{nm} (\epsilon/M^{-1} \text{ cm}^{-1})^a$

[(TMPA)Cu(RCN)] ⁺ (1a)	$[(TMPA)Cu(O_2)]^+$ (1b)	$[{(TMPA)Cu}_2(O_2)]^{2+} (1c)$
343 (5600)	410 (4000)	440 (4000) sh
	500 (1100)	525 (11500)
	580 (1100)	590 (7600) sh
	/4/ (1000)	1035 (160)
[(TMPAE)Cu(RCN)] ⁺ (1a')	$[(TMPAE)Cu(O_2)]^+ (1b')$	$[{(TMPAE)Cu}_2(O_2)]^{2+} (1c')$
342 (4700)	415 (3330)	445 (2000) sh
		532 (9380)
	591 (930)	590 (7000) sh
	760 (950)	nd
$[(D^{I})Cu_{2}(MeCN)_{2}]^{2+}$ (2a)	$[(D^1)Cu_2(O_2)_2]^{2+}$ (2b') ^b	$[(D^1)Cu_2(O_2)]^{2+}$ (2c) ^c
350 (5900/Cu(I))	416 (4500)	450 (1100) sh
		540 (11100)
	583 (1060)	600 (8700) sh
	755 (1110)	1010 (190)

^{*a*} ϵ values given per Cu_nO₂ (n = 1 or 2) moiety; nd = not determined. ^{*b*} This is the 2:2 "open" adduct, eq 8 (see below). The spectrum of the 2:1 superoxo adduct 2b was not independently determined but was taken as the arithmetic mean of those of 2a and 2b'. ^{*c*} After secondary rearrangement ($2c \rightarrow 2d$, see below), we found $\lambda_{max} = 529$ nm, $\epsilon = 9320$ M⁻¹ cm⁻¹; $\lambda_{max} = 436$ nm, $\epsilon = 2000$ M⁻¹ cm⁻¹; $\lambda_{max} = 595$ nm, $\epsilon = 7200$ M⁻¹ cm⁻¹. ^{*d*} The experimental source of the molar absorptivities was either benchtop experiments or kinetic/spectroscopic analyses. Any differences observed were within the error limits.

redox potentials of copper complexes including (a) the flexibility or constraints imposed by chelating ligands, (b) the types of donor atoms, and (c) the geometry of tetracoordinate complexes.⁶³⁻⁶⁷ Here, all the Cu(I) complexes possess identical ligand donor atoms, and so differences could only arise from varying substituents on pyridyl ligand donors. The differences in $E_{1/2}$ values between the three complexes in question are rather small (Table 1). The observed trends are, however, in the expected direction: (1) The moderately electron donating ethyl group of the D^1 ligand linker might be the cause of the slightly more negative redox potential observed in 2a as compared to 1a, while (2) the electron-withdrawing ester group in the meta position relative to the pyridyl-nitrogen donor atom may be responsible for the positive shift in $E_{1/2}$ seen in **1a'** relative to 1a. Similar effects of electron-donating and -withdrawing substituents have been seen in bipyridyl-containing Cu-ligand complexes.68

Low-Temperature Reaction of O₂ with [(TMPAE)Cu-(MeCN)]⁺ (1a') and [(D¹)Cu₂(MeCN)₂]²⁺ (2a). O₂-Uptake Manometry. Experiments were performed at 193 K in propionitrile to confirm the stoichiometry of reaction of O₂ with dinuclear 2a (Experimental Section). The results show absorption of dioxygen by [(D¹)Cu₂(MeCN)₂](ClO₄)₂ [2a-(ClO₄)₂] (0.457 g, 0.45 mmol) in the ratio of Cu/O₂ = 2.14(±0.05); thus, the solution complex is formulated as [(D¹)Cu₂(O₂)](ClO₄)₂ [2c-(ClO₄)₂]. This Cu/O₂ stoichiometry is identical to that of the parent [(TMPA)Cu(RCN)]⁺ (1a) complex.⁴⁵

Reaction of $[(D^1)Cu_2(O_2)](ClO_4)_2$ (2c-(ClO₄)₂) with PPh₃: Quantitative Measurement of the Release of O₂ and Isolation of $[(D^1)Cu_2(PPh_3)_2](ClO_4)_2$. Triphenylphosphine is a good ligand for Cu(I) complexes and has been used to characterize the reactivity of Cu₂-O₂²⁺ species.⁶⁹ At 193 K, $[(D^1)Cu_2(O_2)]$ -(ClO₄)₂ (0.45 mmol) reacted with PPh₃ (0.3 g, 1.1 mmol) to form a copper(I)-PPh₃ complex with concomitant liberation of a gas presumed to be O₂, by analogy to the similar reaction

Scheme 3



with other Cu_2O_2 complexes.^{45,69} The amount of O_2 evolved was quantified by manometry (76% recovery, Experimental Section). The reaction of 2c with PPh₃ proceeds over a 5-6-h period at 193 K. The intense purple color of peroxo-dicopper complex $[(D^1)Cu_2(O_2)]^{2+}$ (2c) diminished, and a light green solution formed. After removal of solvent and recrystallization from acetonitrile-ether, a pale yellow dicopper(I) complex $[(D^1)Cu_2(PPh_3)_2](ClO_4)_2$ was obtained (73% yield) and was characterized by ¹H NMR spectroscopy and C, H, N analysis. The green color observed is presumed to be due to small amounts of oxidized impurities present before the mixture was fractionally recrystallized. Gas-chromatographic analysis of the collected filtrate showed only a trace amount of O=PPh₃ formed. These results suggest that $[(D^1)Cu_2(O_2)]^{2+}$ (2c) is a copper dioxygen complex and that the O-O bond in this species remains unbroken. Thus, the transformations observed for dinuclear 2a in reactions with O_2 and PPh₃ are strictly analogous, Scheme 3, to the chemistry of $[(TMPA)Cu(RCN)]^+$ (1a).⁴⁵

UV-Vis Spectra of O₂ Adducts. Benchtop and Stopped-Flow Determination. In bench-top experiments, reaction of $[(TMPAE)Cu(MeCN)]^+$ (1a') with O₂ in EtCN at 193 K resulted in a rapid change to an intensely purple colored solution. Spectral characteristics agree closely with those observed for oxygenation of $[(TMPA)Cu(MeCN)]^+$ (1a)⁴⁵ (cf. Table 2), corresponding to the 2:1 (Cu/O₂) adduct $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c'). Upon exposure to dioxygen at 193 K, a yellow propionitrile solution of the dicopper(I) $[(D^1)Cu_2(MeCN)_2]^{2+}$ (2a) also rapidly converts to an intense purple color with strong and multiple UV-vis features (Figure S2, supporting information; Table 2). A weaker broad feature, ascribed to d-d transition-(s), is seen at 1010 nm. The formation of the purple species $[(D^1)Cu_2(O_2)]^{2+}$ (2c) is completed by the time the solution of 2a is bubbled with O₂ and inserted into the spectrometer.

Numerical analysis of diode-array stopped-flow measurements shows that the reaction of $[(TMPAE)Cu(MeCN)]^+$ (1a') or

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Figure 3. UV-vis spectra of (a) $Cu/O_2 = 1:1$ intermediates $(---) [(TMPA)Cu(O_2)]^+ (1b), (\cdots) [(TMPAE)Cu(O_2)]^+ (1b'), and (-) [(D^1)Cu_2 - (O_2)_2]^{2+} (2b') and (b) <math>Cu/O_2 = 2:1$ peroxo dicopper(II) species $(---) [\{(TMPA)Cu\}_2(O_2)]^{2+} (1c), (\cdots) [\{(TMPAE)Cu\}_2(O_2)]^{2+} (1c'), (-) [(D^1)-Cu_2(O_2)]^{2+} (2c), and <math>(--) [\{(D^1)Cu_2(O_2)\}_n]^{2n+} (2d)$ generated through numerical analysis of diode-array stopped-flow measurements.

Table 3.	Kinetic I	Parameters for	or O_2	2 Interaction	with	Copper(I)	Compl	lexes	1a, 1	a', an	id 2	2a
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		TMPA ^b (1a)	TMPAE (1a')	D ¹ (2a)
$k_1 (M^{-1} s^{-1})$	183 K 223 K 298 K $\Delta H_1^* (kJ \text{ mol}^{-1})$ $\Delta S_1^* (J \text{ K}^{-1} \text{ mol}^{-1})$	$\begin{array}{c} (1.8 \pm 0.1) \times 10^{4} \\ (9 \pm 4) \times 10^{5} \\ 8 \times 10^{7} \\ 32 \pm 4 \\ 14 \pm 18 \end{array}$	$\begin{array}{c} (8.2 \pm 0.4) \times 10^{3} \\ 4 \times 10^{5 \ c} \\ 4 \times 10^{7 \ c} \\ 31 \pm 5 \\ 5 \pm 29 \end{array}$	$\begin{array}{c} (1.63 \pm 0.01) \times 10^4 \\ (2.0 \pm 0.3) \times 10^5 \\ (4 \pm 1) \times 10^6 \\ 20 \pm 1 \\ -53 \pm 6 \end{array}$
k_{-1} (s ⁻¹)	183 K 223 K 298 K ΔH_{-1}^{*} (kJ mol ⁻¹) ΔS_{-1}^{*} (J K ⁻¹ mol ⁻¹)	8 ± 1 (3 ± 1) × 10 ⁴ 2 × 10 ⁸ 66 ± 4 137 ± 18	$29 \pm 26 \times 10^{4} c4 \times 10^{8} c63 \pm 5132 \pm 29$	$\begin{array}{l} 8.0 \pm 0.2 \\ (6.3 \pm 0.8) \times 10^3 \\ (1.4 \pm 0.5) \times 10^7 \\ 55 \pm 1 \\ 76 \pm 6 \end{array}$
k_2 (s ⁻¹)	183 K 223 K 298 K ΔH_2^* (kJ mol ⁻¹) ΔS_2^* (J K ⁻¹ mol ⁻¹)	$\begin{array}{l} (3.2 \pm 0.2) \times 10^{1 \ d} \\ (2.48 \pm 0.02) \times 10^{2 \ d} \\ (1.8 \pm 0.1) \times 10^{3 \ d} \\ 14 \pm 1 \\ -78 \pm 2 \end{array}$	$(1.52 \pm 0.05) \times 10^{1 d}$ (2.4 ± 0.1) × 10 ^{2 d} (5.8 ± 0.9) × 10 ^{3 d} 21 ± 1 -43 ± 3	$\begin{array}{l} (3.51\pm 0.05)\times 10^1 \\ (3.3\pm 0.1)\times 10^3 \\ (6.8\pm 0.5)\times 10^5 \\ 37\pm 1 \\ -9\pm 2 \end{array}$
$k_{-2} (s^{-1})$ (= k_{off})	183 K 223 K 298 K ΔH_{-2}^{*} (kJ mol ⁻¹) ΔS_{-2}^{*} (J K ⁻¹ mol ⁻¹)	$(1.5 \pm 0.8) \times 10^{-4}$ 0.29 ± 0.04 $(1.2 \pm 0.3) \times 10^{3}$ 61 ± 3 19 ± 10	$\begin{array}{l} (2.1 \pm 0.4) \times 10^{-5} \\ (6.4 \pm 0.4) \times 10^{-2} \\ (7 \pm 1) \times 10^{2} \\ 66 \pm 1 \\ 33 \pm 5 \end{array}$	$\begin{array}{l} (3.9 \pm 0.3) \times 10^{-1} \\ (3.5 \pm 0.2) \times 10^{1} \\ (6.7 \pm 0.9) \times 10^{3} \\ 37 \pm 1 \\ -49 \pm 3 \end{array}$
$k_3 (\mathrm{M}^{-5}\mathrm{s}^{-1})$	183 K 223 K 298 K ΔH_3^* (kJ mol ⁻¹) ΔS_3^* (J K ⁻¹ mol ⁻¹)			$\begin{array}{l} (7\pm2)\times10^{15} \\ (7\pm1)\times10^{14} \\ (5.1\pm0.2)\times10^{13} \\ -21\pm1 \\ -54\pm5 \end{array}$
k_{-3} (s ⁻¹)	183 K 223 K 298 K ΔH_{-3}^{*} (kJ mol ⁻¹) ΔS_{-3}^{*} (J K ⁻¹ mol ⁻¹)			$\begin{array}{c} (2.1 \pm 0.7) \times 10^{-13} \\ (1.4 \pm 0.2) \times 10^{-6} \\ (1.03 \pm 0.05) \times 10^{2} \\ 131 \pm 1 \\ 235 \pm 5 \end{array}$
$k_{on} (\mathbf{M}^{-1} \mathbf{s}^{-1}) (=k_1 k_2 / k_{-1}) (=K_1 k_2)$	183 K 223 K 298 K ΔH_{on}^{*} (kJ mol ⁻¹) ΔS_{on}^{*} (J K ⁻ mol ⁻¹)	$\begin{array}{l} (6.2 \pm 0.5) \times 10^{4 \ d} \\ (6.7 \pm 0.4) \times 10^{3 \ d} \\ (6 \pm 1) \times 10^{2 \ d} \\ -20 \pm 2 \\ -201 \pm 5 \end{array}$	$\begin{array}{c} (4.32\pm 0.08)\times 10^{3\ d} \\ (1.57\pm 0.02)\times 10^{3\ d} \\ (5.2\pm 0.2)\times 10^{2\ d} \\ -10.3\pm 0.2 \\ -170\pm 1 \end{array}$	$\begin{array}{l} (7.1 \pm 0.2) \times 10^4 \\ (1.1 \pm 0.1) \times 10^5 \\ (1.8 \pm 0.2) \times 10^5 \\ 1.7 \pm 0.6 \\ -139 \pm 3 \end{array}$

^{*a*} Standard errors of rate constants were calculated from the results of linear regression analyses for the corresponding activation parameters. Rate constants at intermediate temperatures would therefore generally have smaller associated errors than those at the extreme values of 183 and 298 K. ^{*b*} Values from ref 41. ^{*c*} Relatively uncertain values extrapolated from activation parameters based exclusively on low-temperature data. Calculated uncertainties are close to a factor of 2 at 223 K and 4 at 298 K. ^{*d*} Conditional rate constants based on $[(L)Cu(RCN)^+] = 10^{-3}$ M. True second-order rate constants (M⁻¹ s⁻¹) are obtained by multiplying the values by 10³.

 $[(D^1)Cu_2(MeCN)_2]^{2+}$ (2a) with O₂ initially produces intensely yellow Cu/O₂ = 1:1 superoxo-copper(II) *intermediates* [(TM-PAE)Cu(O₂)]⁺ (1b'), [(D¹)Cu₂(O₂)(EtCN)]²⁺ (2b), and [(D¹)-Cu₂(O₂)₂]²⁺ (2b'), described more fully below. These species possess spectral characteristics similar to those of the superoxo-Cu(II) 1:1 adduct [(TMPA)Cu(O₂)]⁺ (1b) (Table 2), previously observed as an intermediate in kinetic studies.⁴⁰ Band positions and molar absorptivities for the subsequently formed more stable $Cu/O_2 = 2:1$ (peroxo)dicopper(II) products [{(TMPAE)Cu}₂-(O₂)]²⁺ (1c') and [(D¹)Cu₂(O₂)]²⁺ (2c) are very close to the values for [{(TMPA)Cu}₂(O₂)]²⁺ (1c). Calculated spectra of intermediates 1b, 1b', and 2b', based on the kinetic analyses presented in the next section, along with products 1c, 1c', and 2c, are given in Figure 3. Close matching of λ_{max} , ϵ_{max} , and

Table 4. Equilibrium Parameters for O₂ Interaction with Copper(I) Complexes 1a, 1a', and 2a

		TMPA (1a)	TMPAE (1a')	D ¹ (2a)
K_1 (M ⁻¹) (= k_1/k_{-1})	183 K 223 K 298 K $\Delta H_1^{\circ} (kJ \text{ mol}^{-1})$ $\Delta S_1^{\circ} (J \text{ K}^{-1} \text{ mol}^{-1})$	$(1.9 \pm 0.1) \times 10^{3}$ 27 \pm 2 0.34 \pm 0.08 -34 \pm 1 -123 \pm 4	$\begin{array}{l} (2.84 \pm 0.09) \times 10^2 \\ 6.7 \pm 0.4 \\ (9 \pm 1) \times 10^{-2} \\ -32 \pm 1 \\ -127 \pm 3 \end{array}$	$\begin{array}{c} (2.03 \pm 0.04) \times 10^{3} \\ (3.2 \pm 0.1) \times 10^{1} \\ (2.7 \pm 0.3) \times 10^{-1} \\ -35.3 \pm 0.4 \\ -129 \pm 2 \end{array}$
$K_2(-)$ $(=k_2/k_{-2})$	183 K 223 K 298 K $\Delta H_2^{\circ} (kJ \text{ mol}^{-1})$ $\Delta S_2^{\circ} (J \text{ K}^{-1} \text{ mol}^{-1})$	$\begin{array}{l} (2.2 \pm 0.7) \times 10^{5 \ a} \\ (8.6 \pm 1.2) \times 10^{2 \ a} \\ 1.5 \pm 0.4^{a} \\ -47 \pm 3 \\ -97 \pm 10 \end{array}$	$\begin{array}{l} (7 \pm 2) \times 10^{5 \ a} \\ (3.7 \pm 0.3) \times 10^{3 \ a} \\ 8 \pm 2^{a} \\ -45 \pm 1 \\ -76 \pm 6 \end{array}$	$\begin{array}{c} (9.0\pm 0.7)\times 10^{1}\\ (9.5\pm 0.5)\times 10^{1}\\ (1.0\pm 0.1)\times 10^{2}\\ 0.5\pm 0.6\\ 40\pm 3\end{array}$
$K_1K_2 (M^{-1})$	183 K 223 K 298 K ΔH_{12}° (kJ mol ⁻¹) ΔS_{12}° (J K ⁻¹ mol ⁻¹)	$\begin{array}{c} (4.3 \pm 1.5) \times 10^{8 \ a} \\ (2.3 \pm 0.4) \times 10^{4 \ a} \\ (5 \pm 1) \times 10^{-1 \ a} \\ -81 \pm 3 \\ -220 \pm 11 \end{array}$	$\begin{array}{c} (2.1 \pm 0.4) \times 10^{8 \ a} \\ (2.4 \pm 0.1) \times 10^{4 \ a} \\ (7 \pm 1) \times 10^{-1 \ a} \\ -77 \pm 1 \\ -203 \pm 5 \end{array}$	$\begin{array}{c} (1.8 \pm 0.1) \times 10^{5} \\ (3.0 \pm 0.1) \times 10^{3} \\ (2.7 \pm 0.1) \times 10^{1} \\ -34.8 \pm 0.4 \\ -89.3 \pm 1.5 \end{array}$
K_{3}^{b} (M ⁻⁵) (= k_{3}/k_{-3})	183 K 223 K 298 K ΔH_3° (kJ mol ⁻¹) ΔS_3° (J K ⁻¹ mol ⁻¹)			$\begin{array}{l} 3 \times 10^{28} \\ (5 \pm 1) \times 10^{20} \\ (4.9 \pm 0.3) \times 10^{11} \\ -153 \pm 2 \\ -289 \pm 6 \end{array}$

^a Conditional equilibrium constants based on $[(L)Cu(RCN)^+] = 10^{-3} M$. ^b Minor inconsistencies with Table 3 are due to rounding errors.

band shapes indicates nearly identical structural and electronic characteristics in the corresponding superoxo and peroxo complexes.

Results from benchtop and stopped-flow experiments were identical for the more stable 2:1 species $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c') and $[(D^1)Cu_2(O_2)]^{2+}$ (2c). In addition, with 2a, a slow secondary rearrangement from 2c to product(s) 2d, with similar but definitely distinct spectral features, was observed in the temperature range 203-296 K. The nature of this secondary reaction, which is observed exclusively with the dinuclear complex 2a, is detailed in the kinetics part of this contribution.

From the very similar spectral features we deduce analogous trans-(μ -1,2-peroxo)dicopper(II) structures for complexes 1c, 1c', and 2c. We note, however, a small but significant shift of $\lambda_{max} = 540$ nm for $[(D^1)Cu_2(O_2)]^{2+}$ (2c), to $\lambda_{max} = 525$ nm for $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c); a shift in the d-d envelope is also observed (Table 2). We presume this effect to be due to a slightly modified arrangement of the Cu₂-O₂ moiety in 2c with its dinucleating ligand. The detailed kinetics/thermodynamics study of the reaction of O₂ with $[(D^1)Cu_2(MeCN)_2]^{2+}$ (2a) provides considerable insight into the nature of the differences between $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) and $[(D^1)Cu_2(O_2)]^{2+}$ (2c), as described below.

Stopped-Flow Kinetics/Thermodynamics Investigations

Kinetics of Formation of Superoxo-Copper(II) $Cu/O_2 =$ 1:1 Adducts. Reaction of Mononuclear [(TMPAE)Cu-(MeCN)]⁺ (1a'). Table 3 provides a detailed summary of the kinetics of the reactions of $[(TMPAE)Cu(RCN)^+$ (1a') and $[(D^1)Cu_2(RCN)_2]^{2+}$ (2a) with O₂. Rate constants at three temperatures and activation parameters are provided. Published values for [(TMPA)Cu(RCN)]⁺ are included for comparison. Equilibrium parameters, discussed separately below, are provided in Table 4. As implied by the discussions of UV-vis spectroscopy in the previous section, the O₂-binding behavior of 1a' is very similar to that of the parent compound [(TMPA)-Cu(MeCN)]⁺ (1a). Time-dependent UV-vis spectra of the reaction of $[(TMPAE)Cu(MeCN)]^+$ (1a') with O₂, as well as plots of absorbance versus time at 415 and 532 nm, are given in supporting information Figures S3 and S4. The latter plots correlate perfectly with the kinetic model already presented for the reaction of $[(TMPA)Cu(MeCN)]^+$ (1a) with O₂ (Scheme

1),⁴⁰ i.e., eqs 4-6. Clearly, the O₂-binding reactivity of the

$$[(TMPAE)Cu(RCN)]^{+} + O_{2} \frac{\frac{k_{1} \cdot K_{1}}{k_{-1}}}{[(TMPAE)Cu(O_{2})]^{+}} + RCN \quad (eq \ 4)$$

$$\mathbf{1b'}$$

$$[(TMPAE)Cu(RCN)]^{+} + [(TMPAE)Cu(O_{2})]^{+} \frac{\frac{k_{2} \cdot K_{2}}{k_{-2}}}{\mathbf{1a'}}$$

$$\mathbf{1b'}$$

$$[\{(TMPAE)Cu\}_{2}(O_{2})]^{2+} + RCN \quad (eq \ 5)$$

$$\mathbf{1c'}$$

$$\frac{[{(IMPAE)Cu}_2(O_2)]}{1c'} \rightarrow \text{inteversible decay} \quad (eq 6)$$

ester complex [(TMPAE)Cu(MeCN)]⁺ (1a') closely matches that observed for the parent complex [(TMPA)Cu(MeCN)]⁺ (1a), as revealed by comparisons of (i) spectra shown in Figure 4 and (ii) kinetic parameters in Table 3. The metastable 1:1 $Cu-O_2$ superoxo-Cu(II) adduct [(TMPAE)Cu(O_2)]⁺ (1b') forms reversibly ($\lambda_{max} = 415$ nm, $\epsilon = 3330$ M⁻¹ cm⁻¹, Table 2). In the temperature range studied, the "on" rate constant (k_1) is about half of that observed for formation of [(TMPA)- $Cu(O_2)$]⁺ (1b). Conversely, the "off" rate constant k_{-1} for 1b' is twice that for 1b. Since steric effects should not play a role here, this slower formation and faster decay should reflect the difference in redox potentials in complexes 1a and 1a', in which the TMPA ligand slightly favors Cu(II) relative to Cu(I), compared to TMPAE (cf. Table 1).

It is also interesting to compare O₂-binding kinetics with those of another mononuclear copper(I) complex, [(BQPA)Cu]⁺, which preferentially forms a 1:1 adduct for steric reasons.^{40,49} Such hindrances might be expected to influence the approach of O₂, and [(BQPA)Cu(O₂)]⁺ forms much more slowly, with $k_1 = 18 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$ at 183 K.





Figure 4. (a) Plot of $\ln[k_1h/(kT)]$ vs 1/T (k = Boltzmann constant). [{(D¹)Cu₂(MeCN)₂}²⁺]/[O₂]: \Box , 5.06 × 10⁻⁴ M/4.4 × 10⁻³ M; \triangle , 1.28 × 10⁻⁴ M/4.4 × 10⁻³ M; \Diamond , 7.44 × 10⁻⁵ M/4.4 × 10⁻³ M. (b) Plot of $\ln K_1$ vs 1/T. For concentrations, cf. part a. (c) Plot of $\ln[k_2h/(kT)]$ vs 1/T. For concentrations, cf. part a. (d) Plot of $\ln K_1K_2$ vs 1/T. [{(D1)Cu₂(MeCN)₂}²⁺]/[O₂]: \bigcirc , 6.97 × 10⁻⁴ M/4.4 × 10⁻³ M; \square , 3.21 × 10⁻⁴ M/4.4 × 10⁻³ M; \triangle , 1.92 × 10⁻⁴ M/4.4 × 10⁻³ M; \diamondsuit , 6.52 × 10⁻⁵ M/4.4 × 10⁻³ M.

Reaction of Dinuclear $[(D^1)Cu_2(MeCN)_2]^{2+}$ (2a) with O₂. The kinetics of reaction of O_2 with the *dinuclear* complex [(D¹)- $Cu_2(MeCN)_2]^{2+}$ (2a) are even more complicated than those observed for the mononuclear analogues [(TMPA)Cu(MeCN)]⁺ (1a) and [(TMPAE)Cu(MeCN)]⁺ (1a'). However, detailed analysis has allowed us to deduce a rather complete picture, aided by the assumption (and realization) that the basic elements of the behavior of 1a and 1a' should be present in the reaction of 2a with O_2 . Thus, both $Cu(I)/O_2$ 1:1 and 2:1 binding are expected and reactivities of the two individual O2-binding sites in 2a would closely match those of 1a and 1a'. The relevant kinetic scheme is summarized by the reactions shown in eqs 7-11 (Chart 2). In addition one has to take into account that, because of the dinuclear nature of 2a with independently reacting Cu(I) units intermolecular peroxo species analogous to 1c or 1c' will be formed with rate constants close to those observed for 1a and 1a'. Plots of (i) time-dependent UV-vis spectra for $2a + O_2$ at 183 K and (ii) experimental and correlated theoretical absorbance versus time plots at 417 nm (following the formation and decay of 1:1 adducts 2b and 2b') and 540 nm (following the formation of 2:1 adduct 2c) are given as supporting information.42

Initial reaction of O₂ with $[(D^1)Cu_2(MeCN)_2]^{2+}$ (2a) gives rise to 1:1 dioxygen binding similar to $[(TMPA)Cu(O_2)]^+$ (1b) and $[(TMPAE)Cu(O_2)]^+$ (1b'), again best observable at the lowest temperatures. However, the presence of *two* equivalent copper(I) sites available in 2a leads to formation of two such intermediates. Species $[(D^1)Cu_2(O_2)(EtCN)]^{2+}$ (2b) is a 2:1 *open* form (eq 7), having one dioxygen coordinated to one copper ion of the dicopper complex. Thus, it is formally a mixed-valence Cu(I)Cu(II)-superoxo species. Intermediate 2b' is a bis-dioxygen adduct $[(D^1)Cu_2(O_2)_2]^{2+}$, i.e., a 2:2 *open* form,

eq 8. These copper-dioxygen adducts both exhibit identical UV-vis $\lambda_{max} = 416$ nm, with 2b' giving the more intense absorption ($\epsilon = 8900 \text{ M}^{-1} \text{ cm}^{-1}$) since there are twice the number of absorbing chromophores. Intermediates 2b and 2b' cannot be distinguished spectroscopically or kinetically, since the O₂-binding sites are identical and behave independently. 2b' is, however, a necessary species, since its formation inhibits rapid formation of 2c from 2b (eq 9), as especially observed at the lowest temperatures. Thus, while the rate and thermodynamic constants for the initial O₂-binding process (i.e., k_1 , k_{-1} , and K_1 which produces 2b (eq 7) are determined experimentally, the constants k_1' and k_{-1}' (and K_1') (eq 8) were coupled to the former values through statistical factors which led to successful numerical analysis. Specific assumptions and constraints were as follows: (a) The spectrum of 1:1 adduct 2b is the arithmetic mean of the spectrum of the 2:2 complex 2b' and the parent Cu(I) species 2a. (b) $k_1' = 0.5k_1$ and $k_{-1}' =$ $2k_{-1}$. Plots of temperature dependence yielding activation and thermodynamic parameters for k_1 and K_1 , respectively (therefore also providing k_{-1} data), are given in parts a and b, respectively, of Figure 4.

General Observations. For all 1:1 adducts of mononuclear complexes thus far studied [i.e., 1b,⁴⁰ 1b' (Table 3), and [(BQPA)Cu(O₂)]⁺],⁴⁰ O₂-binding (k_{on}) activation enthalpies are significant ($\Delta H_1^{\dagger} = 30-32$ kJ mol⁻¹), while the values ($\Delta H_{-1}^{\dagger} = 63-66$ kJ mol⁻¹) associated with the O₂-off reactions (k_{-1}) are much greater. Somewhat different activation parameters are observed for O₂ on or off binding to the dinuclear complex [(D¹)Cu₂(MeCN)₂]²⁺ (**2a**). ΔH_1^{\dagger} is lower for **2a**, i.e., 20 kJ mol⁻¹ (Table 3). In compensation, $\Delta S_1^{\dagger} = -53 \pm 6$ J K⁻¹ mol⁻¹ for O₂ binding to **2a** (eq 7), while the corresponding value for [(TMPA)Cu(MeCN)]⁺ (**1a**) is $\Delta S_1^{\dagger} = +14 \pm 18$ J K⁻¹

Chart 2



 mol^{-1} (Table 3). An explanation for this more negative activation entropy associated with O₂ binding to dinuclear species 2a is that it reflects the inherently greater number of degrees of freedom for the much bigger and more complex dinuclear complex 2a, and corresponding changes and organization that will occur during the O₂-binding process. Notable, however, is that the accessible temperature range (180–188 K) for the determination of k_1 is rather limited, the associated standard errors of the activation parameters are considerable, and the absolute values of the directly measured rate constants k_1 for 1a and 2a are almost identical, within 90% confidence limits.

Kinetics of Formation of $(\mu$ -Peroxo)copper(II) Cu/O₂ = 2:1 Adducts. Formation of $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c'). As discussed above and illustrated in Figure 3b, the distinctive charge-transfer bands in the UV-vis region observed for $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c') closely match those of the X-ray structurally characterized complex $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c), implicating congruent *trans-*(μ -1,2-peroxo)dicopper(II) structures for both of the species derived from mononuclear precursors [(TMPA)Cu(MeCN)]⁺ (1a) or [(TMPAE)Cu(MeCN)]⁺ (1a').

The final Cu₂O₂ 2:1 (peroxo)dicopper(II) complex [{(TMPAE)-Cu}₂(O₂)]²⁺ (1c') forms by further reversible reaction of [(TMPAE)Cu(O₂)]⁺ (1b') with 1a' (eq 5). Again, while overall similar formation rates (and thermodynamic effects, vide infra) are observed, a detailed examination shows that 1c' is formed up to 15 times more slowly at 183 K than is the "parent" analogue [{(TMPA)Cu}₂(O₂)]²⁺ (1c), Table 3. Differences are less at higher temperatures. In fact, calculated rates are about equal at 298 K. Significantly, "off" values k_{-2} for 1c' are smaller than or equal to those for 1c. The k_{on} (= K_1k_2) value

for $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c') is quite close to that found for the formation of a spectroscopically similar peroxodicopper(II) complex, $[{(BPQA)Cu}_2(O_2)]^{2+}$, for which $k_{on} =$ $(3.2 \pm 0.1) \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ at 183 K.⁴⁰ Investigations of compounds possessing systematically varied electronic properties and steric differences are needed to better understand precisely what contributes to and controls $Cu_n - O_2$ complex formation and stability.



Formation of μ -Peroxo $[(D^1)Cu_2(O_2)]^{2+}$ (2c). Following the formation of the 1:1 adducts 2b and 2b', the ensuing product is the 2:1 closed (μ -peroxo)dicopper(II) complex [(D¹)Cu₂- (O_2) ²⁺ (**2c**) (eq 9), identified by the kinetics (i.e., concentration dependences) and spectral characteristics (vide supra), $\lambda_{max} =$ 540 nm ($\epsilon = 11\ 100\ M^{-1}\ cm^{-1}$), 600 (sh) nm. The gross similarities with $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) and $[{(TMPAE)}^{-}$ $Cu_2(O_2)^{2+}$ (1c') (Figure 3b) suggest that a trans-(μ -1,2peroxo)dicopper(II) intramolecular structure (as depicted in eq 9) is formed, consistent with our examination of hand-held molecular models and the subsequent design of D^1 with its -CH₂CH₂- linker. This complex forms directly from the 2:1 open Cu(I)Cu(II)-superoxo complex [(D¹)Cu₂(O₂)(EtCN)]²⁺ (2b) (eq 9). Very low temperatures and/or excess O₂ inhibits the formation of μ -peroxo **2c** by favoring formation of bis-O₂ intermediate $[(D^1)Cu_2(O_2)_2]^{2+}$ (2b', eq 8), where both copper sites are blocked. The formation of $[(D^1)Cu_2(O_2)]^{2+}$ (2c) is



Figure 5. Comparisons of kinetic and thermodynamic parameters for overall formation of (peroxo)dicopper(II) dinuclear adducts 1c and 2c from copper(I) precursors.

described by the rate and equilibrium constants k_2 , k_{-2} , and K_2 and the second-order rate constant $k_{on} = K_1 k_2$, while $K_1 K_2$ represents the overall equilibrium formation of **2c** from **2a**. Plots for the temperature dependence of k_2 and $K_1 K_2$ are given in parts c and d, respectively, of Figure 4, and the results of numerical analysis giving kinetic and thermodynamic parameters pertaining to **2c** formation are found in Tables 3 and 4.

The *intramolecular* formation of $[(D^1)Cu_2(O_2)]^{2+}$ (2c) is significantly more rapid than for the corresponding 2:1 complexes [{(TMPA)Cu}₂(O₂)]²⁺ (1c) and [{(TMPAE)Cu}₂(O₂)]²⁺ (1c'), the latter being formed in an *intermolecular* fashion from their mononuclear precursors. At 213 K, 2c formation is already beyond the experimental limit (~8 ms) of the stoppedflow instrument. For comparisons, Figure 5 provides pertinent kinetic and equilibrium parameters for 2c formation from dicopper(I) precursor [(D¹)Cu₂(EtCN)₂]²⁺ (2a), and corresponding parameters for [{(TMPA)Cu}₂(O₂)]²⁺ (1c) generation by reaction of mononuclear [(TMPA)Cu(EtCN)]⁺ (1a) with [(TM-PA)Cu(O₂)]⁺ (1b).

Pertaining to the individual kinetic step k_2 (i.e., where a Cu– O₂ 1:1 intermediate attacks a second Cu–EtCN species), there is a substantially higher activation enthalpy for formation of $[(D^1)Cu_2(O_2)]^{2+}$ (2c) (eq 9) relative to $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) (eq 2): $\Delta H_2^{\pm} = 37$ and 14 kJ mol⁻¹ for 2c and 1c, respectively. This is, however, well overcompensated by a dramatic change in activation entropy: $\Delta S_2^{\pm} = -9$ and -78 J K⁻¹ mol⁻¹ for 2c and 1c, strongly favoring formation of 2c over 1c on a kinetic basis.

For direct comparison of the intra- versus intermolecular process occurring in the formation of $[(D^1)Cu_2(O_2)]^{2+}$ (2c) versus $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) or $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c'), Table 3 also provides pseudo-first-order rate constants for k_2 and k_{on} (K_1k_2), calculated at $[{(tripod-ligand)Cu^l(RCN)}^+] = 10^{-3}$ M, since the orders of the overall reactions differ. At the intermediate temperature of 223 K, k_2 and k_{on} are $\sim 13-16$ times greater for the process involving intramolecular 2c formation. The difference is smaller at lower temperatures, while it is greater at higher temperatures. Comparisons between

2c and 1c' formation (Table 3) actually indicate even greater differences in these two systems.

Strong entropic support of intramolecular peroxo formation in **2c** relative to **1c** is also evident from the overall rate constant k_{on} : $\Delta S_{on}^{\dagger} = -139 \text{ J K}^{-1} \text{ mol}^{-1} \text{ vs} -201 \text{ J K}^{-1} \text{ mol}^{-1}$ (cf. Figure 5). This is combined with a small positive activation enthalpy $\Delta H_{on}^{\dagger} = 1.7 \pm 0.6 \text{ kJ mol}^{-1}$ associated with the overall rate constant $k_{on} (=K_1k_2, \text{ Table 3})$, contrary to what is observed for formation of [{(TMPA)Cu}_2(O_2)]^{2+} (**1c**), [{(TMPAE)Cu}_{2-}(O_2)]^{2+} (**1c'**), and [{(BPQA)Cu}_2(O_2)]^{2+}, 40 where negative overall activation enthalpies are found for this composite parameter, since the value of ΔH_{-1}^{\dagger} exceeds that of ΔH_1^{\dagger} and ΔH_2^{\dagger} combined. Thus, for [(D¹)Cu₂(O₂)]²⁺ (**2c**), k_{on} increases with increasing temperature. However, the larger value of ΔH_{on}^{\dagger} (+2 versus -20 kJ mol⁻¹) is suggestive of a structurally "strained" transition state.

An examination of the k_{-2} (= k_{off}) values and associated activation parameters (Table 3) provides further insight into the strained nature of $[(D^1)Cu_2(O_2)]^{2+}$ (2c). These values describe the disruption, i.e., dissociation of O_2 from 2c (eq 9), and they can also be compared to corresponding ones for mononuclear species $[{(TMPA)Cu}_2(O_2)^{2+} (1c) \text{ or } [{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c') (eqs 2 and 5, Figure 5, and Table 3). At 223 K, the rate constant for breakage of one of the copper-oxygen bonds in the Cu-O₂-Cu group of $[(D^1)Cu_2(O_2)]^{2+}$ (2c) giving $[(D^1)$ - $Cu_2(O_2)(EtCN)]^{2+}$ (2b) is 3.5 (±0.2) × 10¹ s⁻¹, ~120 times greater than the corresponding value for $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c), and greater than that found for $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c'). Correspondingly for $2c \rightarrow 2b$ (eq 9), $\Delta H_{-2}^{\dagger} = 37 \pm 1$ kJ mol⁻¹, compared to a range of 61-66 kJ mol⁻¹ for related processes $1c \rightarrow 1b + 1a$, or $1c' \rightarrow 1b' + 1a'$. The negative activation entropy ascribed to this disruptive bond-breaking process for the dinuclear case $[(D^1)Cu_2(O_2)]^{2+}$ (2c) $\rightarrow [(D^1)^{-1}$ $Cu_2(O_2)(EtCN)]^{2+}$ (2b) is $\Delta S_{-2}^{\pm} = -49 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$, suggesting an early transition state where EtCN solvent attacks the intact peroxo-dicopper(II) complex (eq 9), giving the singlemolecule product **2b**. However, the ΔS_{-2}^{\dagger} values are positive, 19 and 33 J K^{-1} mol⁻¹, for the breaking of Cu₂-O₂ moieties composed of mononuclear components, i.e., $1c \rightarrow 1b$ and 1c'

 \rightarrow 1b', respectively, in these cases two molecules (i.e., EtCN and the dinuclear complexes 1c or 1c') combine to form two molecules $[(TMPA)Cu(O_2)]^+$ (1b) (or 1b') plus [(TMPA)Cu-(EtCN)]⁺ (1a) (or 1a').

Thermodynamics. Table 4 provides equilibrium parameters for O₂ binding to mono- or dinuclear copper(I) complexes of TMPA, TMPAE, and D¹.

Superoxo-Copper(II) $Cu/O_2 = 1:1$ Adducts. General observations are that for all 1:1 adducts thus far studied, i.e., $[(TMPA)Cu(O_2)]^+$ (1b), $[(TMPAE)Cu(O_2)]^+$ (1b'), $[(D^1)Cu_2^ (O_2)(EtCN)]^{2+}$ (2b), and $[(BQPA)Cu(O_2)]^+$,⁴⁰ there is a remarkable similarity in the thermodynamics of O2-binding parameters. The stability of dioxygen binding to a single copper(I) ion site is driven by favorable enthalpies ($\Delta H_1^\circ = -32$ to -35 kJ mol⁻¹), but unfavorable entropies ($\Delta S_1^{\circ} = -123$ to -129 J K^{-1} mol⁻¹) preclude observation of Cu-O₂ (and Cu₂-O₂) complexes at ambient temperatures.9

Some individual comparisons are interesting, such as in the relative stabilities of $[(TMPA)Cu(O_2)]^+$ (1b) versus $[(TMPAE)^ Cu(O_2)$]⁺ (1b'). The thermodynamic binding constant K_1 is a factor of 4-7 times less for the latter at low temperatures. As mentioned (vide supra) with reference to the kinetics, since steric effects in binding of O₂ to [(TMPA)Cu(EtCN)]⁺ (1a) versus [(TMPAE)Cu(EtCN)]⁺ (1a') should be unimportant, this variation in K_1 should reflect the slightly more positive Cu(I)/Cu(II) complex redox potential observed for $1a' [E_{1/2} = -608 (1a)]$, -550 mV (1a') in DMF vs Ag/AgNO₃, Table 1];⁷⁰ i.e., there is a smaller driving force toward the redox reaction producing a superoxo-copper(II) product from O_2 and LCu(I).

On the other hand, $[(BQPA)Cu(O_2)]^+$ has a thermodynamic stability $[K_1 = (2.9 \pm 0.3) \times 10^3 \text{ M}^{-1}$ at 183 K, $\Delta H_1^{\circ} = -35$ \pm 6 kJ mol⁻¹, $\Delta S_1^{\circ} = -125 \pm 27$ J K⁻¹ mol⁻¹] quite comparable to that for $[(TMPA)Cu(O_2)]^+$ (1b) or [(TMPAE)- $Cu(O_2)$]⁺ (1b') in spite of the reduced driving force for the oxidation of [(BQPA)Cu]⁺ (relative to **1a** and **1a'**, cf. Table 1; $E_{1/2} = -0.410 \text{ mV}$ in DMF vs Ag/AgNO₃).⁴⁹ Detailed studies on a larger collection of compounds will be required to more fully understand how the formation rates and thermodynamics of copper-dioxygen complexes are controlled by (i) ligand electronic variations and (ii) ligand environment or steric effects.

While thermodynamic parameters K_1 , ΔH_1° , and ΔS_1° for 1:1 O₂ binding to dinuclear $[(D^1)Cu_2(RCN)_2]^{2+}$ (2a) (Table 4) are similar to those observed for [(TMPA)Cu(MeCN)]⁺ (1a) and $[(TMPAE)Cu(MeCN)]^+$ (1a') (Table 4), they are closer to those for 1a; differences between 1a and 2a are, in fact, statistically insignificant. Apparently, the -CH₂CH₂- chain substituent on the 5-position of one pyridyl group in 2a gives a complex more similar to the parent complex 1a (with H in this position) than is the case for 1a', where the electronic structure could be more affected by the 5-ester group (Chart 1). The electrochemically determined redox potentials for the copper(I) complexes 1a, 1a', and 2a (Table 1) support this conclusion; $E_{1/2}$ values for 1a and 2a are quite close, while that for **1a'** is more positive.

As discussed (vide supra) and displayed in Figure 3a (with data given in Table 2), the UV-vis spectra of 1:1 Cu- O_2 intermediates $[(TMPA)Cu(O_2)]^+$ (1b), $[(TMPAE)Cu(O_2)]^+$ (1b'), and $[(D^1)Cu_2(O_2)(EtCN)]^{2+}$ (2b) are similar. While these comparisons suggest that they have the same coordination, the detailed structure of these superoxo-copper(II) species is not known. We have discussed^{40,49,71} the possibilities, i.e., η^2 sideon binding, or "terminal" end-on Cu^{II}-O-O⁻ ligation. The

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(L)Cuterminal', 'end-or

former is known for a superoxo-cobalt(II) complex (formed from O₂ reaction with a Co(I) complex) possessing a sterically demanding hydrotris(3-tert-butyl-5-methylpyrazolyl)borate ligand;⁷² η^2 -O₂ ligation is also observed in Cu(O₂)(HB(3-t-Bu-5-i-Prpz)₃) [HB(3-t-Bu-5-iPrpz)₃ = hydrotris(3-tert-butyl-5-iPrpz)₃) isopropyl)pyrazolylborate].²⁹ Physical-spectroscopic data for these Co and Cu complexes are consistent with the superoxometal(II) formulation; thus, substantial electron transfer from M(I) to O_2 has occurred upon dioxygen binding. An "end-on" coordination is observed in a superoxo-Cu(II) species which is an analogue of TMPA with 6-pivaloylamine substituents on the pyridyl groups; hydrogen bonding by proximal N-H amide groups of this ligand is suggested to stabilize the structure described.³⁰ Analogy to this latter complex and the observed overwhelming tendency for pentacoordination in copper(II) complexes with these kinds of tetradentate ligands⁷¹ would suggest end-on superoxo coordination in $[(TMPA)Cu(O_2)]^+$ (1b), $[(TMPAE)Cu(O_2)]^+$ (1b'), and $[(D^1)Cu_2(O_2)(EtCN)]^{2+}$ (2b). Further structural and spectroscopic studies are needed.

 $(\mu$ -Peroxo)copper(II) Cu/O₂ = 2:1 Adducts. As for the formation of 1:1 adducts, parameters K_2 and $\beta_2 = K_1 K_2$ for formation of μ -peroxo complexes [{(TMPA)Cu}₂(O₂)]²⁺ (1c) and $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c') are quite similar. The TM-PAE adduct 1c' is a factor of ~ 2 less stable at 183 K (Table 4), but at 223 K the values are identical. Also based on values at 183 K, both 1c [$\beta_2 = (4.3 \pm 1.5) \times 10^{11} \text{ M}^{-2}$] and 1c' $\beta_2 =$ $(2.1 \pm 0.4) \times 10^{11}$ M⁻²) are thermodynamically more stable than the quinolyl-substituted 2:1 complexes [{(BPQA)Cu}2- $(O_2)^{2+} [\beta_2 = (1.7 \pm 0.2) \times 10^{10} \text{ M}^{-2}] \text{ or } [\{(BQPA)Cu\}_2(O_2)]^{2+}$ $[\beta_2 = (6 \pm 12) \times 10^6 \text{ M}^{-2}].^{40}$ Again, investigations of compounds possessing well-defined, but systematically varied, electronic properties and steric differences are needed to better understand precisely what contributes to and controls $Cu_n - O_2$ complex formation and stability.

Comparisons of the overall thermodynamics for the reaction

 $2[(TMPA)Cu(RCN)]^{+} + O_2 \rightarrow [\{(TMPA)Cu\}_2(O_2)]^{2+}$ 1a
1c

are most revealing (Figure 5). As expected from the original concept and design of a dinucleating analogue D¹, the intramolecular process provides considerable entropic stabilization of $[(D^1)Cu_2(O_2)]^{2+}$ (2c) compared to $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c), $\Delta S_{12}^{\circ} = -89$ vs -220 J K⁻¹ mol⁻¹. However, no real stabilization of peroxo complex 2c occurs. In fact, ΔG° is less negative for dinucleating ligand complex $[(D^1)Cu_2(O_2)]^{2+}$ (2c) compared to 1c over the entire range 183-298 K, because of the dramatic enthalpic destabilization in forming [(D¹)Cu₂- $(O_2)^{2+}$ (2c) compared to $[{(TMPA)Cu}_2(O_2)^{2+}$ (1c), ΔH_{12}° = -35 vs -81 kJ mol⁻¹, respectively. This overall destabilization of 2c relative to 1c is entirely due to the second step K_2 , which in fact has no significant binding enthalpy $(0.5 \text{ kJ mol}^{-1})$

 $⁽⁷⁰⁾ E_{1/2} = -350$ (1a), -300 mV (1a') in MeCN vs Ag/AgNO₃, unpublished results.

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Figure 6. Kinetics of secondary reaction of $[(D^1)Cu_2(O_2)]^{2+}$ at several temperatures.

for 2c but rather substantial ones, -47 and -45 kJ mol⁻¹, for 1c and 1c', respectively.

As argued, we ascribe the destabilization of $[(D^1)Cu_2(O_2)]^{2+}$ (2c) compared to $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) or $[{(TMPAE)}^{-}$ $Cu_{2}(O_{2})^{2+}$ (1c') to the formation of a "strained" metastable peroxo-dicopper(II) structure 2c. Our design of D1-complex/ O₂ chemistry anticipated that a structure strictly analogous to 1c and 1c' should form, but there are significant differences in the details of the $Cu_2 - O_2$ coordination environment and stability caused by the presence of a -CH₂CH₂- moiety linking the two halves of the molecule. Further evidence for this comes from the differences in vis spectra of 2c, compared to 1c and 1c', Table 2. There is a clear bathochromic shift in the chargetransfer (LMCT) absorption maximum for $[(D^1)Cu_2(O_2)]^{2+}$ (2c) (Figure 4b), $\lambda_{\text{max}} = 540 \text{ nm}$ ($\epsilon = 11 \text{ 100}$), since for [{(TMPA)- $Cu_{2}(O_{2})^{2+}$ (1c) $\lambda_{max} = 525$ nm ($\epsilon = 11500$) and for $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c') $\lambda_{max} = 532 \text{ nm} (\epsilon = 9380)$. We have previously observed significant differences in the chargetransfer band position and intensity in Cu₂-O₂ complexes with variably linked $-(CH_2)_n - (n = 3-5)$ bis[2-(2-pyridyl)ethyl]amine units,⁵⁸ indicating the sensitivity of such absorptions to local environment. A further indication that the coordination environment about the Cu(II) ions in 2c may be altered compared to 1c is that there is a small but significant shift in the position of the d-d bands, $\lambda_{max} = 1010$ and 1035 nm, for 2c and 1c, respectively (Table 2).

The conclusion that $[(D^1)Cu_2(O_2)]^{2+}$ (2c) possesses a strained structure is also borne out by the fact that it is not the ultimate thermodynamic product of reaction of $[(D^1)Cu_2(RCN)_2]^{2+}$ (2a) with O₂, but rearranges to oligomeric peroxo-dicopper(II) products (vide infra).

Formation of Oligomeric Intermolecular μ -Peroxo Copper-Dioxygen Adducts. Over the temperature range 203 K to room temperature, the peroxo-copper product from $[(D^1)-Cu_2(RCN)_2]^{2+}$ (2a) + O₂ is more persistent than is the corresponding analogue $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c), but it is not the same species $[(D^1)Cu_2(O_2)]^{2+}$ (2c) as that seen at low temperature. Figure 6 provides examples of the kinetics of this secondary rearrangement process, at several temperatures. The spectral change monitored is that for 2c with $\lambda_{max} = 540$ nm to species characterized by $\lambda_{max} = 529$ nm and $\epsilon = 9320$ M⁻¹ cm⁻¹ per peroxo unit.

The spectral characteristics indicate that the species formed in this secondary rearrangment also are (peroxo)dicopper(II)

species. The kinetic data can be explained in terms of the relief of the strain in $[(D^1)Cu_2(O_2)]^{2+}$ (2c), as described above. Thermodynamically more stable oligomeric (peroxo)dicopper-(II) complexes can be formed via a corresponding intermolecular process, since the resulting Cu_2-O_2 species no longer suffer from the steric constraints imposed by the $-CH_2CH_2$ – linker, cf. Scheme 4. Such oligomers thus could possess a LMCT absorption close to those found in the unstrained complexes $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) ($\lambda_{max} = 525 \text{ nm}$) and $[{(TMPAE)-Cu}_2(O_2)]^{2+}$ (1c') ($\lambda_{max} = 532 \text{ nm}$), as observed. Thus, one can conclude that, following the rapid formation of 2c, a slower rearrangement occurs via the 2:1 open species $[(D^1)Cu_2(O_2)-$ (EtCN)]²⁺ (2b), whereupon intermolecular reactions (undoubtedly proceeding through intermediates such as Int, Scheme 4) lead to more stable (peroxo)dicopper(II) $\{Cu_2-O_2\}_n$ oligomers, Scheme 4. For a number of other cases in copper-dioxygen complex chemistry, Cu₂-O₂ species formed in an intermolecular fashion from dinuclear precursors have previously been postulated in the literature.^{35,36,73-75} Although detailed structures are not available, partial data for the kinetics of formation are available in one case.^{73,74} A mixed-valent tetrairon $\eta^2:\eta^2$ peroxide-bridged intermediate or transition state has been suggested in the reaction of O₂ with a diiron(II) complex.⁴

The oligomerization process must be quite complex. "Linear" oligomers of varying nuclearity might form. On the basis of the known reactivity of [(TMPA)Cu(RCN)]⁺, such species would not be sufficiently stable at the higher temperatures studied. However, in the stopped-flow kinetic analysis, we have been fortunate to discern that one particular species, a trimer, $[{(D^1)Cu_2(O_2)}_3]^{6+}$ (2d), appears especially stable between 266 and 295 K, and the kinetics and thermodynamics of this reaction, eq 10, could be followed and analyzed. Figure 7 shows the Eyring plot for k_3 , for the rate of formation of the trimer complex 2d, from $[(D^1)Cu_2(EtCN)_2]^{2+}$ (2a) (eq 10). A corresponding plot for the kinetic constant k_{-3} is provided in the supporting information (Figure S5). For temperatures in the above range, the variable concentration and temperature data, as well as the analysis of the individual experiments, strongly suggest trimer formation. None of several other models, specifically invoking dimers and/or monomers only, were compatible with the data. At lower temperatures, larger oligomers appear to be favored, and since these are more strongly concentration dependent, deviations in the behavior of the k_3 plots occur, i.e., conditional rate constants pertaining to high analytical concentrations become larger than those from dilute solutions.

This trimer species $[\{(D^1)Cu_2(O_2)\}_3]^{6+}$ (2d) is remarkably robust and undoubtedly has a closed cyclic architecture; it must be preferentially formed because of some particular stabilization of its structure. A stable "open" form species (e.g., such as **Int**, Scheme 4) with Cu-O₂ moieties at one end is excluded, since (i) characteristic spectra (vide supra) of such Cu/O₂ = 1:1 entities would have been seen, and (ii) they would not be stable at these higher temperatures. "Open" forms (with internal intermolecular μ -peroxo units) but *without* O₂ at the ends, e.g., (RCN)Cu-{(D¹)Cu-(O₂)-Cu(D¹)}_n-Cu(RCN), have also been tested, but their inclusion cannot explain the observed stability of the high-temperature species. We see from Table 4 that the equilibrium constant for formation of **2d** is $K_3 = 3 \times 10^{28} \text{ M}^{-5}$ at 183 K, with $\Delta H_3^\circ = -153 \text{ kJ mol}^{-1}$ and $\Delta S_3^\circ = -289 \text{ J}$ K⁻¹ mol⁻¹.

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Figure 7. Plot of $\ln[k_3h/(kT)]$ vs 1/T, k = Boltzmann constant. For concentrations, cf. Figure 4d.

It is interesting to note that the enthalpy of formation of 2d, when evaluated on the basis of per $Cu/O_2 = 2:1$ moiety, lies between those for the (peroxo)dicopper(II) moieties in the related species $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) and $[(D^1)Cu_2(O_2)]^{2+}$ (2c). The differences in the ΔH° values (Table 4) are substantial and statistically significant. Thus, $\Delta H_{12}^{\circ} = -81 \text{ kJ mol}^{-1}$ for the most (enthalpically) stable unstrained system [{(TMPA)Cu}2- $(O_2)^{2+}$ (1c), but $\Delta H_3^\circ = (-153 \text{ kJ mol}^{-1})/3 = -51 \text{ kJ mol}^{-1}$ per $Cu_2 - O_2$ unit in the trimer complex $[{(D^1)Cu_2(O_2)}_3]^{6+}$ (2d), and $\Delta H_{12}^{\circ} = -34.8 \text{ kJ mol}^{-1}$ for $[(D^1)Cu_2(O_2)]^{2+}$ (2c). Thus, intramolecularly formed (peroxo)dicopper(II) complex 2c is the most strained; it forms rapidly but rearranges to a cyclic trimer in which much, but not all, strain is released relative to that found in the parent system $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c). It is interesting to note that the λ_{max} of the charge-transfer transition for these three species also occurs in the same order, i.e., λ_{max} = 540, 529, and 525 nm for 2c, 2d, and 1c, respectively.

Summary and Conclusions

A detailed understanding of dioxygen interactions with copper(I) centers is important in metal-mediated oxidative transformations of organics, and in the biochemistry of copper, possibly extending to metal-promoted oxygen-radical toxicity. Yet, only a few chemical systems involving well-defined copper complexes have been studied.^{7,9} Here, we have compared

 $\lambda_{max} = 529 \text{ nm}, \epsilon = 9320$ similar to [{(L)Cu}2(O2)]2+ (1c) [(TMPA)Cu(MeCN)]⁺ (1a) with two new complexes, [(TM-PAE)Cu(MeCN)]⁺ (1a') and a dinuclear analogue $[(D^1)Cu_2$ - $(RCN)_2$ ²⁺ (2a). Complex 1a' forms a Cu₂O₂ peroxo adduct with formation and product characteristics nearly identical to that found for **1a**. Our anticipation that a closely related Cu_2 - O_2 peroxo complex would form from 2a was borne out. However, our expectation that the rapidly formed adduct $[(D^1) Cu_2(O_2)$ ²⁺ (2c) would be actually more stable than analogues $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) or $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c') was not borne out. Thus, 1c and 1c' are thermodynamically favored over 2c with the exception of the extrapolated values at 298 K, where entropic contributions are decisive, but all complexes have no significant stability.

Our investigations of the new compounds 1a' and 2a further support our general conclusions^{9,40,41} that the formation of copper-dioxygen adducts is kinetically favorable; in fact, the on rates for O2 binding compare well with those for copperprotein systems.^{40,76} Formation enthalpies indicate strong O₂ binding, in the narrow range $\Delta H_1^{\circ} = -32$ to -35 kJ mol⁻¹ for $Cu/O_2 = 1:1$ complexes [i.e., superoxo-Cu(II) species] with these tripodal tetradentate chelators TMPA, TMPAE, BQPA, and D¹, while $\Delta H_{12}^{\circ} = -50$ to -81 kJ mol⁻¹ for 2:1 Cu₂-O₂ (peroxo)dicopper(II) complexes with TMPA, TMPAE, BQPA, **BPQA**, and four dinuclear complexes $[[Cu_2(R-Xyl)(O_2)]^{2+}]$ employing dinucleating ligands where a tridentate pyridylalkylamino chelate is separated by a 5-substituted (R) m-xylyl spacer.⁴¹ However, the room-temperature stability of all of these copper-dioxygen adducts is precluded by strongly negative reaction entropies, $\Delta S_1^{\circ} = -123$ to -127 J K⁻¹ mol⁻¹ for the 1:1 adducts and $\Delta S_{12}^{\circ} = -145$ to $-250 \text{ J K}^{-1} \text{ mol}^{-1}$ for the 2:1 adducts. As an additional general trend within these series of complexes, more favorable enthalpies are compensated for by less favorable reaction entropies within the ranges cited.

While the kinetic and thermodynamic behavior of 1:1 O₂ binding to $[(D^1)Cu_2(EtCN)_2]^{2+}$ (2a) to form mixed-valent $[(D^1)-$ Cu₂(O₂)(EtCN)]²⁺ (2b) and bis superoxo-copper(II) adduct $[(D^1)Cu_2(O_2)_2]^{2+}$ (2b') follows that seen for [(TMPAE)Cu-(EtCN)]⁺ (1a') \rightarrow [(TMPAE)Cu(O₂)]⁺ (1b') and the others (e.g., complexes of TMPA and BQPA),⁴⁰ the 2:1 binding in the D¹ complex studied here stands in marked contrast. The intramo-

⁽⁷⁶⁾ Andrew, C. R.; McKillop, K. P.; Sykes, A. G. Biochim. Biophys. Acta 1993, 1162, 105-114.

lecular μ -peroxo complex $[(D^1)Cu_2(O_2)]^{2+}$ (2c) is formed from the 2:1 open intermediate $[(D^1)Cu_2(O_2)(EtCN)]^{2+}$ (2b) (eq 9). Entropic factors dominate the kinetics, favoring rapid depletion of 2a and formation of 2c over a wide range of temperatures. Both the kinetic activation entropies (for k_2 , $\Delta S_2^{\dagger} = -9$ J K⁻¹ mol⁻¹, and for k_{on} , $\Delta S_{on}^{\dagger} = -139 \text{ J K}^{-1} \text{ mol}^{-1}$) and overall thermodynamic entropy of formation (i.e., for K_1K_2 , $\Delta S_{12}^{\circ} =$ -89 J K⁻¹ mol⁻¹) are considerably more favorable than what is seen in corresponding values for the mononuclear analogues TMPA, TMPAE, BQPA, BPQA,⁴⁰ and dinuclear [Cu₂(R-Xyl)- (O_2)]^{2+,41} vide supra. Thus, we succeeded in designing a structural analogue of $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c), as seen by the spectroscopic similarity of 2c and 1c, and we have overcome a sizable fraction of the large entropic handicap (i.e., $\Delta S_{12}^{\circ} =$ -220 J K^{-1} mol⁻¹ for 1c) in the Cu₂-O₂ complexes formed from mononuclear precursors. However, our design of D¹ was not perfect, since it presents severe drawbacks in terms of the strain and weakened bonds of the derived $Cu_2 - O_2$ mojety in $[(D^1)Cu_2(O_2)]^{2+}$ (2c), with a quite small $\Delta H_{12}^{\circ} = -35 \text{ kJ mol}^{-1}$, compared to the $\Delta H_{12}^{\circ} = -81$ kJ mol⁻¹ for 1c formation [or even compared to $\Delta H_{12}^{\circ} = -50$ to -81 kJ mol⁻¹, the entire range we have observed for many other compounds (vide supra)]. As discussed, the strain manifests itself in (i) vis spectral shifts seen for the Cu_2-O_2 moiety, compared to 1c or 1c'; (ii) facilitated breaking of one Cu-O bond, i.e., favorable k_{-2} (eq 9) and associated ΔH_{-2}^{\dagger} value compared to 1c or 1c'; and (iii) eventual complete conversion of $[(D^1)Cu_2(O_2)]^{2+}$ (2c) to intermolecular (peroxo)dicopper(II) $[{(D^{1})Cu_{2}(O_{2})}_{n}]^{2n+}$, which are less-strained oligomers.

These oligomers were also characterized by $\lambda_{max} = 529$ nm, a value much closer to that found in Cu₂-O₂ complexes formed from mononucleating ligands TMPA and TMPAE, namely, $[{(TMPA)Cu}_2(O_2)]^{2+}$ (1c) or $[{(TMPAE)Cu}_2(O_2)]^{2+}$ (1c'). The *intermolecular* nature of the Cu₂-O₂ moieties in these oligomers allows relief of steric strain, providing the driving force for their formation. A particularly stable cyclic trimer species $[{(D^1)Cu_2(O_2)}_3]^{6+}$ (2d) was identified; it possesses a ΔH_3° of formation (-51 kJ mol⁻¹ on a per Cu₂-O₂ basis), making it less strained than its precursor 2c, but still more strained than 1c ($\Delta H_{12}^{\circ} = -81$ kJ mol⁻¹).

Thus, the Cu₂-O₂ μ -peroxo complex (or complexes) containing D¹ is (or are) in fact more stable than those found for mononucleating ligands TMPA or TMPAE. However, it is not the naively expected *intramolecular* species $[(D^1)Cu_2(O_2)]^{2+}$ (**2c**), but rather highly associated Cu₂-O₂ compounds formed in an *intermolecular* fashion, species that cannot possibly form with ligands like TMPA and TMPAE. A lesson from the

present investigation is that there exists the possibility, or even the probability, that secondary rearrangements occur in reactions of dioxygen with dinuclear metal complexes, and that one must consider *intermolecularly* formed metal dioxygen species, in terms of analysis and interpretation of observed physical and spectroscopic properties, or reactivity patterns. In fact, evidence for such species for other copper^{35,36,74,75} and iron⁴ complexes already exists.

The future design of ligands that could lead to unstrained and stabilized structures is a challenge, not only to produce copper-dioxygen complexes which might have room-temperature stability but also to further amplify upon and test some of the notions or observations coming from this study. For example, how much entropy advantage can be generated in a dinucleating ligand, and are there other ways to do this? How much strain (i.e., loss of enthalpic stabilization) can one afford in order to favor the intramolecular μ -peroxo complex relative to other species? Knowledge of how to control or build in strain is of interest for tuning of dioxygen binding affinities, promoting enhanced reactivity (i.e., of peroxo-metal complexes) toward substrates, and in devising systems that could be catalytic (i.e., with turnover) in their O₂ reactions. Future investigations will address such issues, but will also include examination of synthetic variations of simpler mononuclear systems, to enhance our further basic understanding of how ligand electronic influences and steric factors control copper(I)/dioxygen reactivity.

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Supporting Information Available: Figures S1–S5 with ¹H NMR spectra of D¹ and $[(D^1)Cu_2(MeCN)_2]^{2+}$ (**2a**) at 298 and 230 K (S1), low-temperature benchtop UV–vis spectra at 193 K in propionitrile (S2), time dependence of the UV–vis spectra in the reaction of $[(TMPAE)Cu(MeCN)]^+$ (**1a**') with O₂ (S3), absorbance vs time plots at 415 and 532 nm for the same reaction (S4), and an Eyring plot for k_{-3} (S5) (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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