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Supplementary Material Available: Synthetic experimental details for compounds **4a**, **4b**, and **7**, X-ray experimental data for **7**, and tables of atomic thermal factors, atomic positional parameters, bond distances, and angles for **7** (22 pages); listing of observed and calculated structure factor amplitudes for **7** (24 pages). Ordering information is given on any current masthead page.

Formation of a Copper–Dioxygen Complex (Cu_2–O_2) Using Simple Imidazole Ligands

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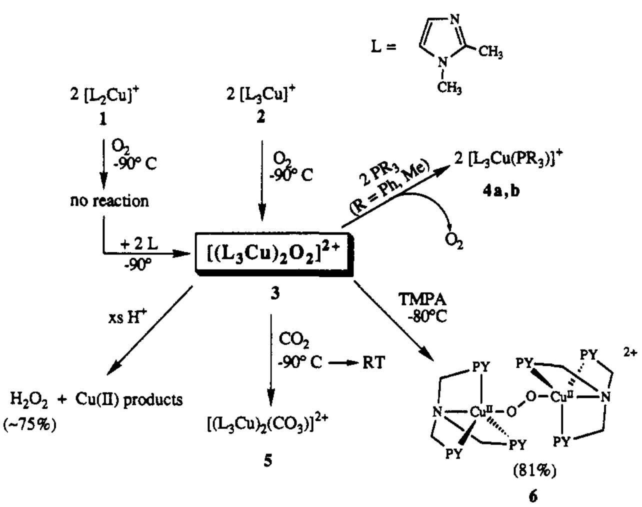
Side-chain imidazole ligation (derived from histidine) pervades the active-site chemistry of copper metalloproteins, including the O_2-carrier hemocyanin (Hc),[1] in addition to copper oxygenases and oxidases.[2] In bioinorganic modeling studies, there has been considerable recent progress in the characterization of synthetically derived $\{Cu_2–O_2\}$ species,[2a,3–5] but these systems have generally not utilized imidazole ligands. There is a good deal of interest in polyimidazole copper complexation,[6,7] and here we report that a $\{Cu_2–O_2\}$ species can be generated by reaction of O_2 with a mononuclear Cu(I) complex possessing the simple unidentate 1,2-dimethylimidazole (L) ligand.

Scheme I



Following Sorrell's observation that linear two-coordinate Cu(I) complexes (with nitrogen heterocyclic ligands) are unreactive to CO and O_2,[8] we observed a similar phenomenon with $[L_2Cu^I](PF_6)$ (**1**).[9] However, when another equivalent of L is added to form $[L_3Cu^I](PF_6)$ (**2**),[10] derived solutions are extremely air sensitive. By then employing low-temperature manipulations that have been successfully applied to copper(I) complexes with aminoalkylpyridine polydentate ligands,[5,11] we found that oxygenation of **2** at −90 °C in CH_2Cl_2 (manometry: Cu:O_2 = 2.06 ± 0.02) gave a stable, EPR-silent (77 K), intensely brown colored solution [UV-vis λ_{max} (ϵ, M^{-1} cm^{-1}), 346 (sh, 2200),[12] 450 (sh, 1450), 500 (1900), and 650 (600) nm], formulated as the peroxo–dicopper(II) complex $[\{L_3Cu\}_2(O_2)]^{2+}$ (**3**) (Scheme I).

Reactivity studies have been found to be useful in characterizing copper–dioxygen complexes,[13] and here they provide further evidence for the presence of a bound nucleophilic peroxo moiety. Reaction of tertiary phosphines PR_3 (R = Ph, Me) displaces the bound O_2 ligand in **3**, as judged by the qualitative detection of dioxygen using pyrogallol,[11] and by the isolation of $[L_3Cu(PR_3)]^+$ (**4**).[14] Reaction of **3** with an excess of acid ($HPF_6 \cdot Et_2O$, 10 equiv/Cu) generates H_2O_2 in ~75% yield as determined by iodometric titration. Also consistent with a peroxo–metal formulation,[13a,b] complex **3** undergoes an immediate reaction with CO_2 at low temperature (−90 °C), which upon warming produces a carbonato–dicopper(II) complex $[\{L_3Cu\}_2(CO_3)](PF_6)_2$ (**5**).[15]

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(10) $[L_3Cu^I](PF_6)$ (**2**): Anal. Calcd for $C_{15}H_{24}CuF_6N_6P$: C, 36.24; H, 4.88; N, 16.92. Found: C, 36.67; H, 5.11 N; 16.97. Λ_m (CH_3CN) = 144 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte).

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(14) The reaction of **3** with PPh_3 was slow and yielded $[L_3Cu^I(PPh_3)](PF_6)$ (**4a**) (yield = 67%) with a small amount of $OPPh_3$ (7%). Anal. Calcd for $C_{33}H_{39}CuF_6N_6P_2$: C, 52.16; H, 5.13; N, 11.06. Found: C, 51.51; H, 5.12 N; 10.76. With PMe_3 the reaction of **3** was fast and yielded 81–85% of $[L_3Cu^I(PMe_3)](PF_6)$ (**4b**), which was proved by ^1H NMR.

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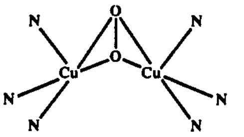
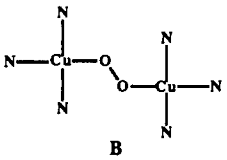
Further striking evidence for the formulation of $[\{L_3Cu\}_2(O_2)]^{2+}$ (**3**) and verification that it contains a bound O_2^{2-} ligand comes from its reaction with TMPA (TMPA = tris[(2-pyridyl)methyl]amine), which is known to form a purple *trans*-μ-1,2-peroxo-bridged dicopper(II) complex (**6**) when $[(\mathrm{TMPA})\mathrm{Cu}^{\mathrm{I}}(\mathrm{RCN})]^+$ is reacted with O_2 at −80 °C.[5,16] We observe that addition of TMPA (−90 °C) to the brown solution of **3** instantaneously transforms it to a purple solution with spectral features identical with those of **6** (Scheme I); the yield of this conversion is 81% based on the established spectrum of **6**.[16] We attribute this "peroxide transfer" reaction to the lability of unidentate L and the greater stability of the chelating TMPA ligand complex. This may prove to be an example of a dynamic "self-assembly" process[17] utilizing a "preformed" Cu_2O_2 core.

The structure of $[\{L_3Cu\}_2(O_2)]^{2+}$ (**3**) (CH_2Cl_2, 100 K) has been probed by X-ray absorption spectroscopy.[18] Edge comparisons with $[L_3Cu^{\mathrm{I}}](PF_6)$ (**2**) indicate that **3** is a Cu(II) complex.[19] Simulation of the EXAFS[18] required four first-shell O/N ligands to account for the intensity of the first shell in the FT, while outer shell atom single and multiple scattering contributions from the imidazole rings alone were not sufficient to account for the intensity of the second shell in the FT. This extra intensity required either a Cu–Cu interaction or an O atom at 2.85 Å. The data could be interpreted by either of two models (A or B) shown herein.[18] Structure A contains a bent μ-η^2:η^2-peroxo ligand, a bridging mode seen in acetylene-bridged dicopper(I) complexes;[20] structure A is also closely related to that proposed for other $\{Cu_2\text{–}O_2\}$ complexes previously described.[5] Kitajima and coworkers have structurally characterized a dicopper(II) complex with a planar μ-η^2:η^2-peroxo group.[4] Model B possesses a planar Cu(II) coordination and has a *trans*-μ-1,2-peroxo group as is seen in **6**.[21]





	A	B
Cu-N (equatorial)	2.01 Å	2.01 Å
Cu-N(axial)	2.24 Å	
Cu-O(1)	1.92 Å	1.88 Å
Cu-O(2)	1.92 Å	2.85 Å
Cu-Cu	2.84 Å	4.30 Å

In conclusion, it is possible to generate a copper–dioxygen complex by using a simple imidazole ligand, by sufficiently lowering the temperature, thus thwarting further irreversible reduction (e.g., $Cu{:}O_2 = 4{:}1$)[22] or disproportionation. This observation is reminiscent of the behavior observed for simple iron(II) porphyrins in their 1:1 O_2 binding.[23] Interestingly, the obvious difference in properties of $[\{L_3Cu\}_2(O_2)]^{2+}$ (**3**) and those of oxyhemocyanin (e.g., λ_{max} = 350 nm (ϵ, 20000); Cu···Cu = 3.56 Å)[1b] suggests that **3** does not possess a $\{Cu_2\text{–}O_2\}$ core structure like that observed in the protein, again illustrating the multiple structures possible for copper–dioxygen species.[5,13a,b] Further studies will be directed toward additional characterization of **3** and synthetic modifications.

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Supplementary Material Available: Details of the data collection and data analysis (2 pages). Ordering information is given on any current masthead page.

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(15) $[\{L_3Cu\}_2(CO_3)](PF_6)_2$ (**5**): Anal. Calcd for $C_{31}H_{48}Cu_2F_{12}N_{12}O_3P_2$: C, 35.32; H, 4.56; N, 15.94. Found: C, 35.24; H, 4.76 N; 15.42. UV–vis (CH_2Cl_2): λ_{max} 360 (ϵ 1940), 712 (350). IR (Nujol): ν(PF) = 840 cm^{-1}, ν(CO) = 1255 cm^{-1}. EPR silent (CH_2Cl_2, 77 K). Λ_m (CH_3CN) = 250 Ω^{-1} cm^2 mol^{-1}.

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(21) At this time, we favor model B as the more plausible structure for $[\{L_3Cu\}_2(O_2)]^{2+}$ (**3**) because it possesses a reactivity pattern similar to that seen for **6**.[13a,b]

(22) At room temperature, complex **2** takes up oxygen with the stoichiometry of $4Cu{:}1O_2$, suggesting a four-electron reduction of O_2 to give oxo–copper(II) species.

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Chemoenzymatic Synthesis of Optically Active (Meth)acrylic Polymers

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Optically active polymers possess many interesting properties and have found applications in asymmetric syntheses, as chiral adsorbents for separation of racemates, and in liquid crystals.[1] A new approach to their synthesis would expand the scant arsenal of existing methods.[1] Recently, lipase-catalyzed asymmetric polycondensations have been explored for the production of optically active polyesters,[2] but the reaction rates and molecular weights obtained have been disappointing due to a plummeting reactivity of the enzymes toward higher molecular weight substrates.

Following our proposal to resolve racemic alcohols by using them as nucleophiles in asymmetric transesterifications catalyzed by lipases in neat organic solvents[3] (instead of conventional lipase-catalyzed, asymmetric hydrolysis of racemic esters in water[4]), this new strategy has become popular for the resolution of racemic alcohols,[5] as well as such other nucleophiles as amines,[6] thiols,[7]

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