

Formation, spectroscopy and reactivity of the $[L_3Cu^II_2Cu^III O_2]^{3+}$ core: A new structural motif in copper dioxygen chemistry

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Interaction of copper with dioxygen is of importance in both industrial oxidation processes and biological systems. Thus discrete complexes resulting from reactions of Cu(I) complexes and dioxygen are of great interest. Mononuclear and binuclear copper dioxygen complexes have been known for some time. Herein we report the characterization of a novel class of trinuclear complexes generated using simple diamine ligands and Cu(I). A 3:1 LCu(I):O₂ stoichiometry leads to complete 4 e⁻ reduction of O₂. Crystallographic, spectroscopic, and theoretical investigations are consistent with the formation of a localized mixed-valence [Cu^{II}Cu^{II}Cu^{III}] core. This 3:1 metal:O₂ stoichiometry is unprecedented not only for copper but for any transition metal. A complete spectroscopic characterization and the reactivity of these complexes towards exogenous substrates will be presented.

