Dioxygen–Copper Reactivity: A Hydroperoxo–Dicopper(II) Complex

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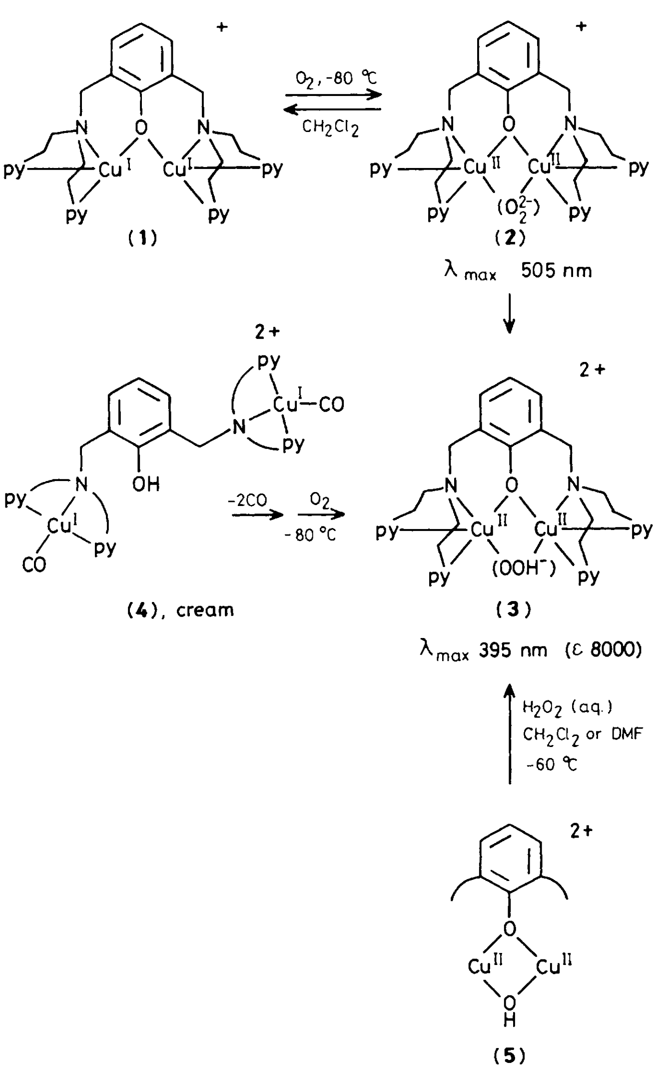
A hydroperoxo–dicopper(II) complex (**3**) can be prepared by (a) direct protonation of a peroxo–dicopper(II) complex (**2**), (b) oxygenation of a ligand-protonated form of the dicopper(I) precursor of (**2**), and (c) reaction of hydrogen peroxide with a hydroxo-bridged dicopper(II) complex (**5**); (**3**) reacts quantitatively with triphenylphosphine or tetrahydrothiophene to give (**5**) and oxygenated products.

In investigations of the reactions of dioxygen (O_2) with copper(I) complexes,[1–6] we have reported that when a solution of a phenoxo-bridged dicopper(I) compound, $[Cu_2(L–O^-)]^+$ (**1**, py = 2-pyridyl), is exposed to O_2 at low temperature (<-60 °C) in dichloromethane, a purple ($\lambda_{max.}$ 505 nm) peroxo–dicopper(II) complex (**2**) (*i.e.*, dioxygen–copper adduct), is formed reversibly.[2,6,7] Here, we show that a protonated form of the dioxygen complex (**3**) can be generated by several synthetic approaches. To our knowledge, this is the first reported example of a hydroperoxo-like complex of copper.

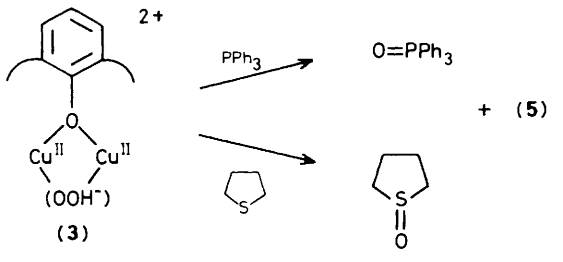
The peroxo-complex (**2**), which is known to possess either a terminally co-ordinated or an asymmetrically bridged peroxo-copper(II) moiety[8,9] can be protonated directly using HBF_4–Et_2O in CH_2Cl_2 at -80 °C to produce the green e.s.r.-silent species (**3**). A spectrophotometric titration experiment can be carried out in which the acid is added to the purple solution of (**2**) whereupon the initial absorption at 505 nm is reduced in intensity and a strong characteristic absorption at 395 nm (ε 8000 dm^3 mol^{-1} cm^{-1}) grows in. An isosbestic point is observed indicating that only two species are involved in this protonation reaction and thus (**2**) is directly converted into (**3**).



A second approach involves the addition of dioxygen to the dicopper(I) complex (**4**), $[Cu_2(L–OH)(CO)_2](PF_6)_2$,† which contains the same dinucleating ligand (L–OH), but in the protonated form. The carbonyl ligands can be removed from (**4**) under reduced pressure (0 °C) and then cooling the CH_2Cl_2 solution to -80 °C followed by exposure to O_2 results in the rapid conversion into (**3**), as indicated by the u.v.–visible spectrum and the observed stoicheiometry of dioxygen uptake (manometry at -80 °C; Cu : O_2 = 2 : 1). Thus, the phenol group serves as a stoicheiometric source of H^+ and protonates a putative dioxygen adduct of the decarbonylated form of (**4**) to give (**3**).

Another method by which (**3**) may be generated is by the addition of an exesss of aqueous hydrogen peroxide to a dichloromethane and/or dimethylformamide (DMF) solution of the phenoxo- and hydroxo-bridged dicopper(II) complex (**5**), $[Cu_2(L–O^-)(OH)]^{2+}$.[3a] This reaction results in a change in the absorption due to (**5**)[3a] ($\lambda_{max.}$ 378 nm, ε 3500 dm^3 mol^{-1} cm^{-1}) to produce the strong absorption maximum at 395 nm which is characteristic of (**3**). This method of generating (**3**) provides further support that this complex contains a peroxidic moiety.

We observe an interesting difference in the reactivities of the peroxo complex (**2**), and the hydroperoxo compound (**3**). The addition of triphenylphosphine (PPh_3) to (**2**) results in the simple displacement of the dioxygen (peroxo-) ligand liberating O_2 quantitatively.[6] By contrast, (**3**) reacts with 1 equiv. of either PPh_3 or tetrahydrothiophene to give essentially quantitative yields of O=PPh_3 or tetrahydrothiophene *S*-oxide; the copper product produced (also quantitatively) in both cases is (**5**). These results suggest that protonation of a



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† Satisfactory elemental analyses were obtained; i.r. data: ν(CO)(KBr) 2080 cm^{-1}; ν(OH) 3525 cm^{-1}.

dioxygen–copper complex may result in 'activation' *via* the formation of a hydroperoxo-like complex which is capable of transferring an oxygen atom to a substrate while leaving behind a stable hydroxo-copper(II)$_n$ moiety. Further mechanistic work is required to distinguish between a metal based reaction or a pathway involving displacement of the coordinated HO_2^- ligand followed by its direct reaction with a substrate.[10]

Transition metal hydroperoxo species are well established as important intermediates in the oxidation of hydrocarbons.[11,12] A copper–hydroperoxo-species has been hypothesized as being an important intermediate in the catalytic reaction of the copper mono-oxygenase dopamine-β-hydroxylase,[13] and has also been proposed to be involved during the disproportionation of superoxide (O_2^-) catalysed by the copper–zinc superoxide-dismutase.[14] Thus, complex (**3**) may be of relevance to active site intermediates in these and other copper proteins involved in dioxygen activation.

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