

Activation of Dioxygen by Cu^I Complexes containing 2,2'-Bipyridine or 1,10-Phenanthroline and 2-Methylimidazole

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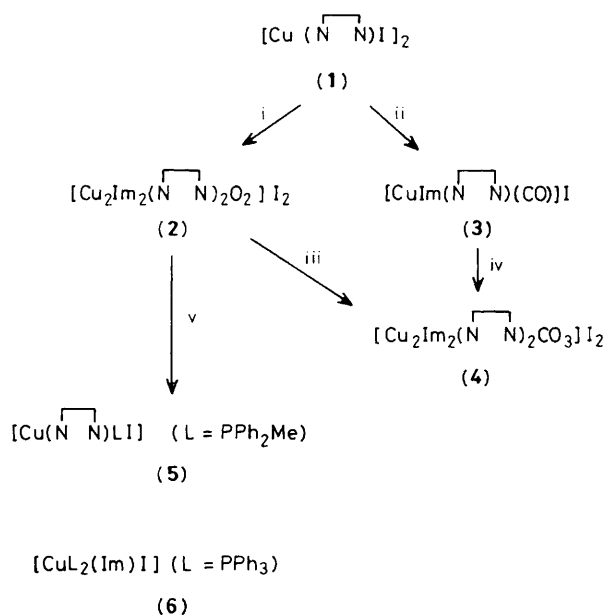
The isolation and characterisation of an oxygen adduct of a copper(II) complex containing chelating *N*-heterocycles and 2-methylimidazole is reported.

Activation of oxygen by Cu^I complexes is of interest as a model for hemocyanin.¹ Spectroscopic evidence^{2–4} has established that the active site in hemocyanin contains two copper centres, bridged in the oxygenated form by a dioxygen molecule and by an oxygen atom donor. In this paper, we report the isolation and characterisation of an oxygen adduct of a copper(II) complex containing chelating *N*-heterocycles (2,2'-bipyridine or 1,10-phenanthroline) and 2-methylimidazole (Im). It is one of the very few examples of a stable Cu^{II} peroxo complex.⁵ Acetonitrile solutions of [Cu₂(\overline{NN})₂I₂] (1) (\overline{NN} = 2,2'-bipyridine or 1,10-phenanthroline) undergo rapid and irreversible oxygen absorption in the presence of stoichiometric quantities of Im [in a 2.5 : 1 Im : (1) molar ratio]. The peroxo species [Cu₂(\overline{NN})₂Im₂O₂]I₂ (2) thus formed precipitates out of solution. It is characterised on the basis of its analytical and conductivity data [Λ 80 (ohm)⁻¹ in 10⁻³ M dimethylformamide, DMF], i.r. and e.s.r. spectroscopy, and polarographic experiments as well its reactions with oxygen acceptors such as PR₃. The oxygen absorption of (1) in the presence of stoichiometric quantities of Im has been followed by gas volumetric analysis in dry DMF or MeCN at 25 °C. Oxygen uptake established that two copper atoms are necessary to absorb one molecule of oxygen as indicated in Scheme 1. The compound (2) on acidification with HClO₄ in MeCN generated H₂O₂ which was unambiguously detected by cyclic voltammetry. Thus cyclic voltammetry of an acidified

MeCN solution of compound (2) containing 0.1 M Buⁿ₄N⁺ ClO₄⁻ gave an irreversible reduction wave at -1.02 V (vs. standard calomel electrode, s.c.e.) which was identical to that of a standard MeCN solution of H₂O₂ of the same concentration. On repeated scanning, the voltammetric peak at -1.0 V (vs. s.c.e.) due to H₂O₂ decreased on each scan with a concomitant increase of a peak at -0.72 V (vs. s.c.e.) owing to water reduction. The generation of H₂O₂ with acid, as well as the presence of a band at 1150 cm⁻¹ in the i.r. spectrum of (2), established the compound as a Cu^{II} peroxide complex. Such acid treatment of peroxobridged complexes to form H₂O₂ has been reported previously.⁶ Conductance measurements on (2) in dry DMF indicated a 1 : 2 electrolyte which is in agreement with our formulation.

The e.s.r. spectrum of compound (2) recorded at 93 K in frozen MeCN solution provides additional support for its structure. The intensity of a low field line at 1600 G,[†] which clearly indicates a dimeric structure, decreases dramatically with increase in temperature. This demonstrates that the copper atoms in the dimeric complex are exchange coupled with a triplet ground state.⁷ An alternative explanation involving dissociation of the dimer seems unlikely in view of the electrochemical experiment. Attempts to grow a single

[†] 1 G = 10⁻⁴ T



Scheme 1. Reagents: i, Im, O_2 , MeCN; ii, Im, CO, CH_2Cl_2 ; iii, CO, MeCN; iv, O_2 ; v, PPh_2Me or PPh_3 , CH_2Cl_2 .

crystal of (2) for X-ray structural analysis have failed so far because of its low solubility in organic solvents.

Compound (2) on reaction with CO gave a highly insoluble material which was established as a carbonate (4) on the basis of its i.r. spectrum (bands at 1720 and 1250 cm^{-1} characteristic of a bidentate carbonate) and analytical data. Interestingly, the same compound (4) was obtained by treating (1) with CO in presence of stoichiometric quantities of Im [Im : (1) 2.5 : 1] to produce (3), which on further reaction with O_2 gave (4) (Scheme 1). The formulation of (3) is proposed on the basis of its i.r. spectrum which had a peak at 2090 cm^{-1} and conductivity data which indicated a 1:1 electrolyte. The ability of the precursor of (2) i.e. $[\text{Cu}(\text{N} \equiv \text{N})\text{ImI}]$, to bind CO to

give (3) is analogous to that of deoxy hemocyanin which reacts similarly.⁸ All attempts to isolate (3) resulted in decarbonylation which is characteristic of copper(I) carbonyl species.⁹ Addition of a stoichiometric or an excess quantity of L ($\text{L} = \text{PPh}_3$ or PPh_2Me) to a solution of (2) in dry CH_2Cl_2 resulted in the formation of the corresponding phosphine oxide, as established by h.p.l.c. The copper complexes (5) and (6) that are formed in these reactions were isolated and characterised by elemental analysis, conductivity, and n.m.r. spectroscopy (Scheme 1).

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