Notes

Reaction between 1,3-Diphenylisobenzofuran and a Blue Oxyhaemocyanin Model Compound

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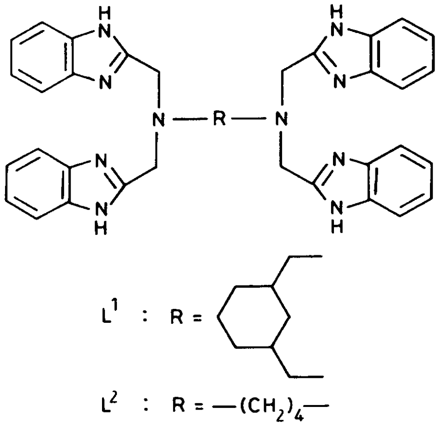
Deep blue species derived from the binuclear copper(I) complex with 1,4-bis[*N*,*N*-bis-(2-benzimidazolylmethyl)amino]butane (L^2) and O_2 exhibited high reactivity towards 1,3-diphenylisobenzofuran, an efficient singlet $O_2(^1\Delta_g)$ scavenger. This gave indirect evidence for O_2-complex formation in the deep blue solution.

Several authors have attempted to prepare model compounds for oxyhaemocyanin, however there is no binuclear copper(I) complex which becomes blue when oxygenated and shows direct evidence for the reversible formation and cleavage of copper–oxygen bonds at ambient temperature.[1–5]

In a previous paper,[6] we reported that the solution (CH_3CN–CH_3OH 14:1, v/v) of binuclear copper(I) with L^1 (shown below) provides a function characteristic of haemocyanin, *i.e.* the reversible colour change: colourless in the absence of O_2 and deep violet in the presence of O_2 near ambient temperature (3—10 °C). We could not, however, obtain direct evidence for the formation of the dioxygen complex in terms of the resonance-Raman measurements, which may be due to the instability of the violet species towards the laser beam.



In this article we have investigated the reaction between 1,3-diphenylisobenzofuran (dpbf) and the coloured oxyhaemocyanin model compounds in order to obtain indirect confirmation for O_2-complex formation in solution.

Experimental

Materials.—$[Cu^I(CH_3CN)_4]BF_4$ was prepared according to the general method.[7] The ligands L^1 and L^2 were prepared according to the method described by Nishida and co-workers.[6,8] 1,3-Diphenylisobenzofuran was obtained commercially (Tokyo Kasei, Co. Ltd.).

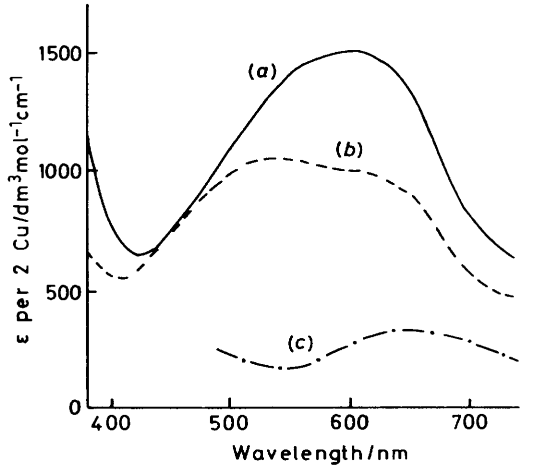


Figure 1. Absorption spectra of complexes with L^2(3 °C). (*a*) Cu^I–L^2–O_2 (15 min bubbling with O_2) in CH_3CN–CH_3OH (14:1, v/v), (*b*) Cu^I–L^2–O_2 (5 min bubbling with O_2) in CH_3OH, and (*c*) Cu^{II}–L^2 in CH_3OH [$Cu(NO_3)_2\cdot3H_2O$ + L^2]

Reaction between Dioxygen and the Copper(I) *Complex.*—Under an atmosphere of nitrogen, the stoicheiometric amount of $[Cu^I(CH_3CN)_4]BF_4$ was added to the ligand solution (L^1 or L^2) (100 cm^3, [ligand] = 1×10^{-3} mol dm^{-3}) which was cooled in an ice-bath (3 °C) to yield a cream-yellow solution. Oxygen gas was bubbled through the solutions at 3 °C. The absorption spectra of the resulting solutions were measured.

Reaction between dpbf and Coloured Species.—To the coloured solutions, obtained as described above, was added powdered dpbf (20 mg) and absorption spectra measurements were performed on these solutions.

Results and Discussion

The solutions of $[Cu^I(CH_3CN)_4]BF_4$ and ligand are almost colourless, or pale yellow, under an N_2 atmosphere.[6] When O_2 was bubbled into the mixture of $[Cu^I(CH_3CN)_4]BF_4$ and L^2, the colour changed to deep blue; the absorption spectrum of the blue species is given in Figure 1. It is clear that new absorption bands appear in the range 500—700 nm, and the intensities (ε per 2 Cu > 1 000 dm^3 mol^{-1} cm^{-1}) are distinctly different from

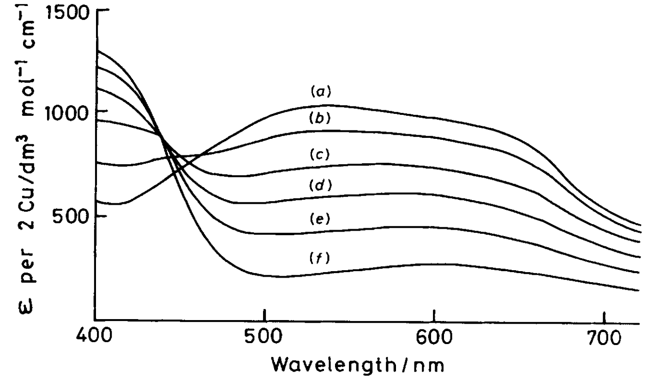


Figure 2. Time course of absorption spectra of blue species of Cu^I–L^2–O$_2$ system in CH$_3$OH. (*a*) Cu^I–L^2–O$_2$ (5 min bubbling with O$_2$) at 3 °C, (*b*) 1 h after solution (*a*) was exposed to air at 3 °C, (*c*) 3 h after at 3 °C, (*d*) 6 h after at 3 °C, (*e*) 12 h after at ambient temperature, and (*f*) 24 h after at ambient temperature

those of the pale green copper(II) complex of L^2 (see Figure 1). This indicates that these strong absorption bands should not be attributed to the *d–d* transitions of copper(II) species. No radical was detected in the e.s.r. spectrum of the blue solution.

The time course of the absorption spectrum of the Cu^I–L^2–O$_2$ system is shown in Figure 2. This blue species is relatively stable at 3 °C, and gradual decomposition occurs after 1 h [see Figure 2(*b*)]. After 24 h, the solution turned green; the absorption spectrum of this solution resembles that of the copper(II) complex in the visible region.

When dpbf was added to the blue solution of the Cu^I–L^2–O$_2$ system, decomposition of the blue species was greatly accelerated, *i.e.* the solution turned green within 1 h and the absorption spectrum resembled that of the green solution in Figure 2(*f*). Similar features were observed for the violet solution of the Cu$^I_2$–L^1–O$_2$ system. Addition of dpbf caused the sudden disappearance of the absorption bands around 560—650 nm[6] of the violet solution. When the blue solution of the Cu$^I_2$–L^2–O$_2$ system was added to the dpbf solution, decomposition of dpbf was observed, *i.e.* decrease of the absorption band at 414 nm (ε 24 700 dm^3 mol^{-1} cm^{-1})[9] was detected. These observations suggest that dpbf reacts with the coloured oxyhaemocyanin model compounds.

1,3-Diphenylisobenzofuran is known to be an efficient singlet oxygen($^1\Delta_g$) scavenger, but its reactivity towards triplet oxygen (^{3}O$_2$) and H$_2$O$_2$ is low.[9] According to Chan[10] and our recent work,[11] dpbf is highly reactive towards oxygen complexes, including the peroxide adducts of binuclear iron(III) and mononuclear Cr^{VI}, Mo^{VI}, and V^V species. Based on these facts, we conclude that the high reactivity of the coloured species studied here towards dpbf should be attributed to the presence of a dioxygen complex in solution. This is consistent with the spectral results described before.

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