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A Solid Dioxygen Derivative of Phthalocyaninatoiron (II)

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When phthalocyaninatoiron(II), ‘FePc’, reacts with O_2 in conc. H_2SO_4* there is a reversible addition of dioxygen, followed by an irreversible oxidation of the species formed [1]. The final product obtained is phthalimide, which can be isolated by precipitation with water.

In a kinetic study of the reaction [2], the composition S–PcFe–O_2–FeP$_c$–S (S = HSO_4^-) was assigned to the spectroscopically reversible species. More recently, we observed that FePc also reversibly interacts with O_2 in dimethylsulphoxide (DMSO) [3]. However, the spectroscopically reversible oxygenated species is unstable; the reaction solution readily discolours and a precipitate forms. We now report characterisation of this solid and its identification as PcFe–O_2–FePc, a species similar to that often suggested to be an intermediate in the oxidation of Fe-porphyrins, but which has never been isolated [4].

When O_2 is bubbled into a solution of FePc in DMSO under N_2, the spectrum typical of a bis-adduct, PcFe(DMSO)$_2$ (λ_{max} 653 nm) [5] changes to give one with λ_{max} 625 nm, with formation of isosbestic points (Fig. 1A). Although the process is reversible, this reversibility critically depends on the temperature and the concentration of PcFe [3].

The absorption band generally decreases in intensity and a readily isolable precipitate, ‘S’, forms when O_2-bubbling is carried out in a hot, concentrated solution of PcFe.

By way of contrast, when PcFe is coordinated to dimethylformamide (DMF), sterically hindered N-bases (*e.g.* α-picoline, ‘α-pic’, 2-methylimidazole, ‘2-MeIm’) or highly volatile bases (*e.g.* *n*-propylamine), interaction with O_2 does not lead to formation of a new species in solution. Only the precipitate ‘S’ is obtained. The same compounds (*i.e.* ‘S’), mixed with α-PcFe, is given when H_2O is added to a solution of PcFe in conc. H_2SO_4 in air.

Whatever the method of preparation, ‘S’ does not contain solvent molecules. That it indeed contains dioxygen is proven by the fact that a solution of ‘S’ in conc. H_2SO_4 (under N_2) gives the same absorption spectrum as the reversible oxygen species formed in this solvent (*i.e.* SPcFeO$_2$FePcS) reported previously [1, 2]. Further N_2-bubbling into this solution leads to the spectrum of PcFe. The formula PcFe–O_2–FePc for S deduced from this behaviour in H_2SO_4 was confirmed by elemental analysis: calcd. for $C_{64}H_{32}N_{16}Fe_2O_2$, C 65.77, H 2.77, N 19.17, O 2.75; found, C 65.8, H 2.8, N 19.2, O 2.6 (these results are an average of several analyses). The i.r. spectrum has medium-intensity bands at 820, 840, and 890 cm^{-1}, not present in α- and β-PcFe. Several other bands in the spectrum (characteristic of PcFe) show small shifts to lower frequencies.

A variable-temperature magnetic moment determination showed that the compound is strongly antiferromagnetic, μ = 2.0 BM at r.t., 0.6 BM at 30 K.

PcFe–O_2FePc does not coordinate weak bases such as DMSO (which explains the instability of the reversible oxygen species when the reaction PcFe + O_2 is carried out in this base), DMF, α-pic, and 2-MeIm. When shaken with these bases (or solutions of them) it slowly turns green in colour and an absorption spectrum of a bis-adduct is obtained, *i.e.* the Fe–O_2–Fe bond is broken.

By way of contrast, PcFe–O_2–FePc readily coordinates strong bases (*e.g.* py, γ-pic, Im) to give blue solutions having spectra with $\lambda_{max} \simeq 625$ nm, which then turn green in colour ($\lambda_{max} \simeq 655$ nm), *i.e.* the bis-adducts are given quantitatively [5, 6] (Fig. 1B). These adducts are readily isolated from solutions. The blue solutions become more stable on successive dilution with an inert solvent. Thus, evaporation of solvent from a 0.5% solution of n-propylamine in benzene gives unaltered (X-ray powder diagram, i.r.) PcFe–O_2FePc.

Although the Fe–O_2–Fe bond is unstable in solution, PcFe–O_2–FePc appears to be quite stable in the solid state up to 250 °C (t.g.a.).

Under some preparative conditions, the interaction PcFe + O_2 in solution led (irreproducibly) to a solid ‘B’, which appears to be a crystalline modification of PcFe–O_2–FePc. Thus, ‘B’ had the same composition as PcFe–O_2–FePc (chemical analysis) and the same spectra in H_2SO_4 and solutions of bases (ϵ_{623} about the same for ‘B’ and ‘S’ in 0.5% solutions of n-propylamine in benzene). However, there are marked differences between the two compounds in the solid state. The i.r. spectrum of ‘B’ has no bands in the region 800–1000 cm^{-1}, assignable to dioxygen [7]; the spectrum is identical to that of α-FePc. The X-ray powder diagrams of B and α-FePc are also identical.

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*In this medium FePc is implicitly assumed to be tetraprotonated (see refs. 1).

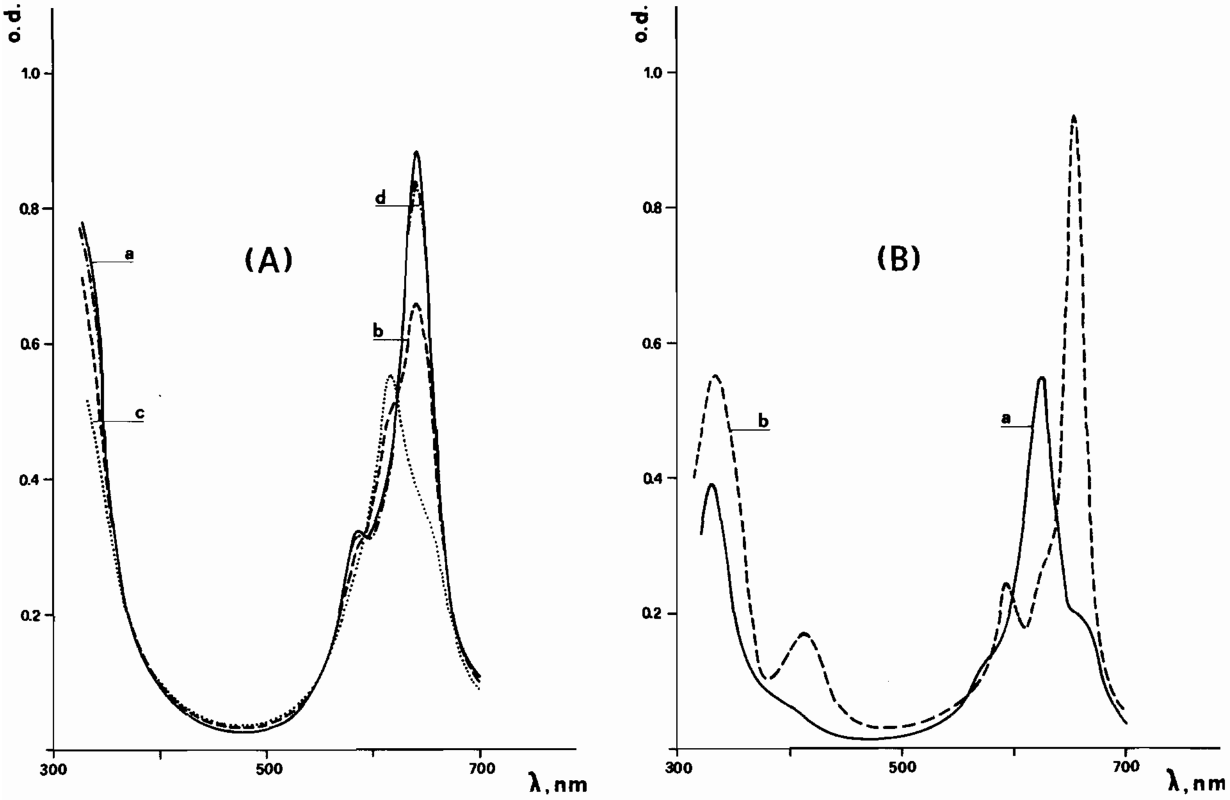

Fig. 1. Absorption spectra: A. FePc in degassed (N_2)DMSO (c = 1.1 × 10^{-4} mol dm^{-3}, 1 mm cell, T = 20 °C) a); b) after bubbling in O_2 for 30 min; c) as for b), 90 min; d) after bubbling in N_2 for *ca.* 24 h. B. PcFe–O_2FePc in py (c = 4.0 × 10^{-5} mol dm^{-3}, 1 mm cell); a) 30 min after mixing; b) *ca.* 24 h after mixing.

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