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Photoreactivity of μ-Oxobis(phthalocyanatoiron(III)) and μ-Oxobis(phthalocyanatomanganese(III))

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The probable existence of polynuclear manganese species in the oxidation of water to oxygen in plant photosynthesis [1, 2] has prompted studies of the redox and photoredox reactivity of binuclear manganese complexes [3, 4].

The complex μ-oxobis(phthalocyanatomanganese(III)) (I) [5–7] has been reported to be photoreduced in pyridine, under vacuo, if the pyridine is not 'carefully dried' [3, 8]. As part of our studies on this molecule in connection with the oxygenation of phthalocyanatomanganese(II), PcMn(II), [8] we have re-investigated its photochemistry, and extended the study ot newly synthesized iron(III) analogs.

Experimental

Electronic spectra were recorded on a Hitachi-Perkin Elmer model 340 spectrophotometer. Magnetic moments were recorded with a fully automatic Faraday balance of published design [9]. Quantum yields were determined by chemical actinometry with Reinecke's Salt [10]. The amount of photoreaction was determined by monitoring the decrease in the Q band of the compounds. Visible light was obtained *via* a 600 watt quartz halogen lamp and using appropriate narrow band interference filters to irradiate the Soret or Q band region. PcMc–O–MnPc was prepared from twice sublimed Pc(II)Mn using published procedures [7]. Imidazole (Eastman) was twice recrystallised from benzene. Tetra(alkylsulphonamido)phthalocyanineiron(II) complexes were prepared using published procedures [11]. μ-Oxobis(tetraoctylsulphonamidophthalocyanineiron(III)), $(\text{ToPcFe(III)})_2\text{O}$ (VII), and μ-Oxobis(tetradodecylsulphonamidophthalocyanineiron (III)), $(\text{TdPcFe(III)})_2\text{O}$ (VI) were prepared by chromatography of the iron(II) precursors on alumina, eluting with 5% methanol in chloroform or 5% methanol in dichloromethane. Use of the pure chlorinated solvents led only to elution of the iron(II) precursors themselves.

Anal. Calcd. for $(\text{ToPcFe(III)})_2\text{O}$: C, 57.21; H, 6.45; N, 12.51. Found: C, 57.2; H, 6.7; N, 12.8%. $\lambda_{max}(\log\epsilon)$ in THF 636 nm (4.54) 333 nm (4.64). Calcd. for $(\text{TdPcFe(III)})_2\text{O}\cdot 4\text{CH}_2\text{Cl}_2$: C, 56.74; H, 6.79; N, 9.68. Found: C, 56.8; H, 7.0; N, 9.7%. λ_{max} $(\log\epsilon)$ in THF 633 nm (5.34) 333 nm (5.36).

Analysis by: Canadian Microanalytical Service Ltd., Vancouver, B.C. Magnetic data for $(\text{TdPcFe(III)})_2\text{O}$. The following data are of low accuracy because the very small 'pull" is offset by a large diamagnetic correction: Temp. K, χ'_m, μ B.M.: 352.8, 1.39×10^{-3}, 1.98; 334.8, 1.50×10^{-3}, 2.00; 277.7, 1.65×10^{-3}, 1.91; 166.8, 2.07×10^{-3}, 1.67; 124.4, 2.50×10^{-3}, 1.58; 98.8, 2.57×10^{-3}, 1.43; 79.9, 1.91×10^{-3}, 1.10.

Results and Discussion

Manganese Systems

Complex (I) is unstable in dimethylacetamide (DMA) or dimethylformamide (DMF) *in vacuo,* to yield a mixture of mononuclear manganese(II) and manganese(III) phthalocyanines [8], which under the influence of visible light are cleanly photoreduced to PcMn(II) [3, 8, 12]. In rigorously dried pyridine, under vacuo, species (I) is indefinitely stable in visible light, including sunlight. However, we confirm that if traces of water are present (py:water:5000:1) then PcMn(II)(Py)_2 is generated but with low quantum yield (ϕ = 10^{-3}). It is known that, thermally, complex (I) reacts with water in pyridien, slowly to yield PcMn(III)OH (II) via cleavage of the Mn–O–Mn bond [8]. This complex (II) is readily photoreduced with visible light to PcMn(II) and it is likely that the photoreduction of (I), in wet pyridine, proceeds via (II). Hydroxyl ion probably acts as the electron donor. Proof of this conjecture is difficult to obtain because of the very low quantum yield.

It had been reported [13] that irradiation of alkaline solutions of tetrasulphonatophthalocyanatomanganese(III), TsPcMn(III), results in the formation of the corresponding TsPcMn(II) species. An alkaline solution of the binuclear complex (I) in ethanol ([KOH] 10^{-2} in EtOH, [1] 10^{-5}) is indefinitely stable in the dark, but photoreduces with white light to a hydroxymanganese(II) phthalocyanine species-(III), probably $(\text{PcMn(OH)}_2)^{2-}$ (III) (Fig. 1) cleanly, but with a small quantum yield (*ca.* 10^{-2}). This same species, (III), may be prepared from reaction of PcMn(II) with KOH/EtOH *in vacuo*. Species (III) is only stable in the presence of excess $[\text{OH}^-]$ and could not be isolated in a pure state for analysis. Both these solutions, whether prepared photochemically or from manganese(II), return to complex (I) when exposed to atmospheric oxygen (slowly, *ca.* 50%

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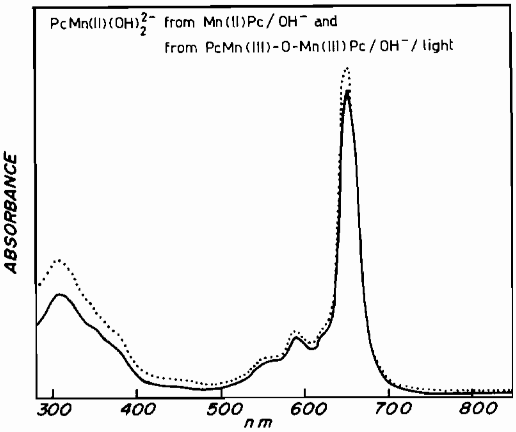

Fig. 1. The electronic spectrum of the species believed to be $(OH)_2Mn(II)Pc^{2-}$ obtained from visible light irradiation of complex (I) (solid line) or from reaction of PcMn(II) with NaOH (hatched line), both in ethanol.

transformation after 24 h 10^{-5} *M* solution). Previously Harriman and co-workers have demonstrated very low quantum yield photoreductions of manganese(III) porphyrin species [14, 15] in parallel with this work. Low yields are probably a consequence of low lying charge transfer bands [16] which 'waste' the energy available to this system.

Iron Systems

Preparation

Recently Ercolani and co-workers [17] have identified μ-oxobis(phthalocyanatoiron(III)) (IV), analogous to (I), and confirmed through gas uptake, magnetism and infrared analysis employing oxygen-18. We note that Collamati prefers a μ-peroxo bridged formulation for this species [18], but believe that the weight of evidence favours the Ercolani oxy bridged structure.

During our photochemical studies with long chain sulphonamido phthalocyanines [11], tetra(dodecylsulphonamido)phthalocyanatoiron(II) TdPcFe(II) (V) was investigated. This could be purified by chromatography on neutral alumina eluting the green product with pure chloroform. If, however, this product was eluted with 5% methanol in chloroform, the chromatographic band turned blue and a ferric complex now identified as μ-oxobis(tetra(dodecylsulphonamido)phthalocyanatoiron(III)) $(TdPcFe(III))_2O$ (VI) is isolated. The identity of this species is confirmed by electronic and vibrational spectroscopy, and magnetism. The Q band of species (VI) appears at 633 nm considerably blue shifted relative to mononuclear metal phthalocyanines and similar to the species (IV) discussed above, and to the binuclear manganese analog (I).

The presence of a μ-oxo bridge is also indicated by comparing the FTIR spectrum of this species, with its precursor (V) (Fig. 2). There is clearly an additional band at 810 cm^{-1}. Ercolani and co-workers demonstrated the presence of a band at 850 cm^{-1} in the unsubstituted PcFe(III)–O–Fe(III)Pc which shifted down to 801 cm^{-1} upon substitution with oxygen-18. An extra band lying in the region 800–900 cm^{-1} is typical of an Fe–O–Fe deformation mode [19]. The magnetic moment of species (VI), (2.0 BM at 298 K) and its marked temperature dependence (see Expt.) is essentially identical to that of the Ercolani μ-oxo species (IV) and characteristic of high spin iron(III) coupled through oxygen [19].* A companion species μ-oxobis(tetraoctylsulfonamidophthalocyanatoiron(III)), was prepared in a similar fashion and exhibited a moment of 1.7 BM at 298 K.

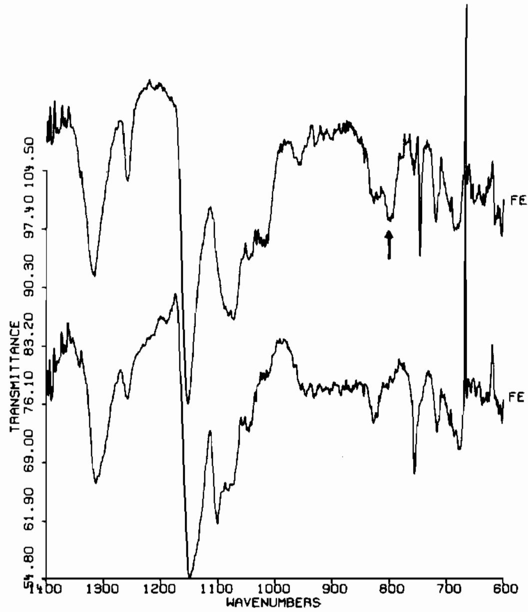

Fig. 2. The Fourier Transform Infrared Spectra of TdPcFe(III)–O–Fe(III)TdPc (VI) and TdPcFe(II) (V). (Powder dispersed on a filter paper support)

Photochemistry

Although the ferric complexes do not fluoresce and must possess low lying d–d transitions (intra t_{2g} (in O_h) transitions), they are nevertheless photoactive, albeit with low quantum yield. The μ-oxo species (VI) cleanly photoreduces when irradiated, under nitrogen, into its Q band in DMF or THF solution, to yield the iron(II) precursor (V) with ϕ = 0.01 (Fig. 3). This reaction is carried out at low concentrations of metallophthalocyanine (*ca.* 10^{-5}–10^{-6} *M*) and it is not clear what is being oxidised,

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*In view of the very large molecular weight, and very large diamagnetic correction, the magnetic susceptibility values cannot be regarded as highly accurate. We have therefore not attempted a detailed analysis of these data.

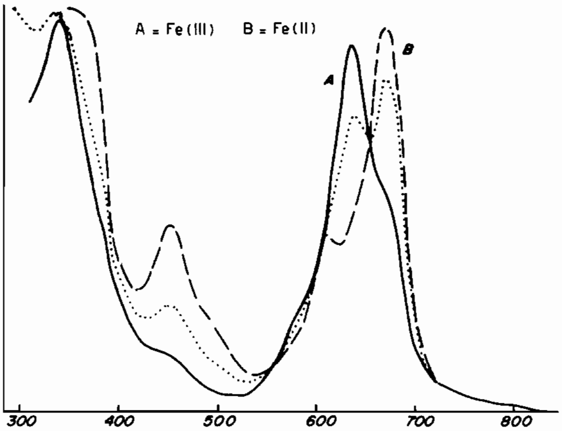

Fig. 3. Photoreduction of TdPcFe(III)–O–Fe(III)TdPc (VI) dissolved in DMF using visible light. Solid line, complex (VI). Long hatched line, complex (V) product. Dotted line, intermediate mixture of both Fe(III) (VI) and Fe(II) (V) species.

presumably solvent or an expeditious impurity. Indeed, it is not proven that this is a true photochemical reaction rather than a photochemically assisted thermal reaction. However, it is pertinent to note that the M(III) state is very strongly stabilised in these μ-oxo species (by as much as 700 mv) [20, 21]. If light causes a cleavage of the M–O–M bond, then the mononuclear species so formed are very powerful oxidising agents. The redox couple for mononuclear TdPcFe(III)/TdPcFe(II) is at 600 mV (DMF, TEAP), providing considerable driving force for reduction if cleavage can be achieved. Note that while visible light irradiation causes reduction from iron(III) to iron(II), ultraviolet light (254 nm) can cause further reduction to iron(I) [22], though with very low quantum yield. Probably the low quantum yields observed here are a consequence of a very short lived photoactive state which decays to lower lying d–d states.

The μ-oxo species (VI) is sensitive to coordinating electron donors such as imidazole, 2-methylimidazole and dimethylamine, all of which cause reduction to adducts of the precursor iron(II) complex (V), even under an oxygen atmosphere. With imidazole, for example, under pseudo first order conditions, in dry DMF, and under nitrogen, at 25 °C, reduction to $(Im)_2Fe(II)TdPc$ occurs with a first order rate constant of $k_0 = 1.3 \times 10^{-5}\ s^{-1}$ (Figs. 4, 5). The identical species can be prepared by direct reaction of imidazole with iron(II) complex (V). It is clear from previous studies [23] that strongly donor ligands shift the Fe(III)/Fe(II) redox potential cathodically thereby favouring reduction to Fe(II).

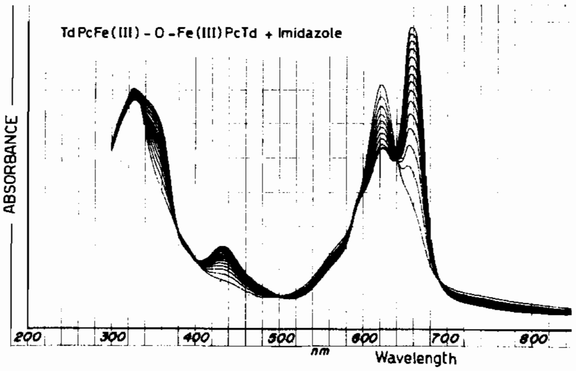

Fig. 4. Reaction of TdPcFe(III)–O–Fe(III)TdPc (VI) with imidazole in DMF at room temperature. Successive time spectra, half-life about 15 h $[Fe] = 1.03 \times 10^{-5}$ $[Im] = 3.65 \times 10^{-2}$ *M*.

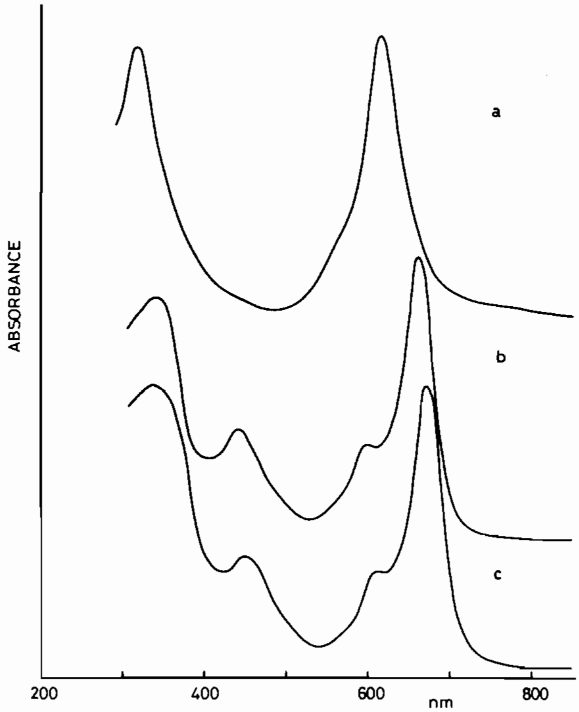

Fig. 5. The spectra, in DMF, of a) TdPcFe(III)–O–Fe(III)-TdPc (VI), b) TdPcFe(II) (V) and c) $TdPcFe(II)(Imidazole)_2$.

The manganese μ-oxo species (I) reacts with oxygen to form an oxygen adduct [8], there is no such observable reaction with the iron analog (VI). Under nitrogen or vacuo, the manganese species (I) disproportionates and is eventually reduced to manganese(II) phthalocyanine. The iron oxo species (VI) is also reduced to iron(II) phthalocyanine (V), in DMF under vacuo. However, this reaction is several orders of magnitude slower than the manganese species (I) disproportionation under comparable conditions, and an order of magnitude slower than the imidazole reduction, cited above. Since these reactions are monitored at concentrations near 10^{-5} *M*, and it is difficult even in 'dry' solvents to reduce water concentrations below 10^{-4} *M*, we believe that this reduction occurs as a consequence of slow hydrolysis of the solvent generating basic product which facilitate reduction of the iron(III) complex.

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