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New Dioxygen Complex of Manganese Phthalocyanine

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Summary The formation of a dioxygen complex of manganese phthalocyanine in poly(2-methyl-1-vinylimidazole)-*NN*-dimethylformamide solution has been demonstrated by e.s.r. and electronic spectra for the first time.

It has been reported that manganese phthalocyanine (Mn-Pc) in pyridine (Py) binds oxygen¹ and that the μ -oxo dimer (*i.e.*, Py-Mn-Pc-O-Mn-Pc-Py) is formed as the final oxygen-containing product.² In the absence of globin, haem of haemoglobin itself is also oxidized irreversibly to a μ -oxo dimer, in a process which is believed to proceed *via* a dioxygen complex.³ Here, the first spectroscopic evidence for the O₂-adduct of Mn-Pc is presented.

Electronic absorption spectra of Mn-Pc were studied in *NN*-dimethylformamide (DMF) containing poly(2-methyl-1-vinylimidazole) (PMVIm) at room temperature. By adding PMVIm the solubility of Mn-Pc was increased, thus avoiding its aggregation in DMF. In the absence of O₂, the main absorption band of Mn-Pc in PMVIm (1%)-DMF was observed at 672 nm. When O₂ was introduced, a new absorption maximum appeared at 710 nm, while the band at 672 nm disappeared in a few minutes. The species which gave the band at 710 nm was stable at least for a few days at room temperature. In the absence of PMVIm, the absorption maximum appeared at 672 nm without O₂ and shifted to 710 nm on addition of O₂. Seemingly the interaction between Mn-Pc and O₂ does not depend on the presence of PMVIm.

The e.s.r. spectra of Mn-Pc in PMVIm (1%)-DMF were measured at 77 K (Figure). In the absence of PMVIm, an attempt to observe the e.s.r. absorption for Mn-Pc (+O₂) in DMF was unsuccessful owing to the low solubility of Mn-Pc for the e.s.r. measurements. The spectrum of Mn-Pc before the introduction of O₂ is shown in the Figure

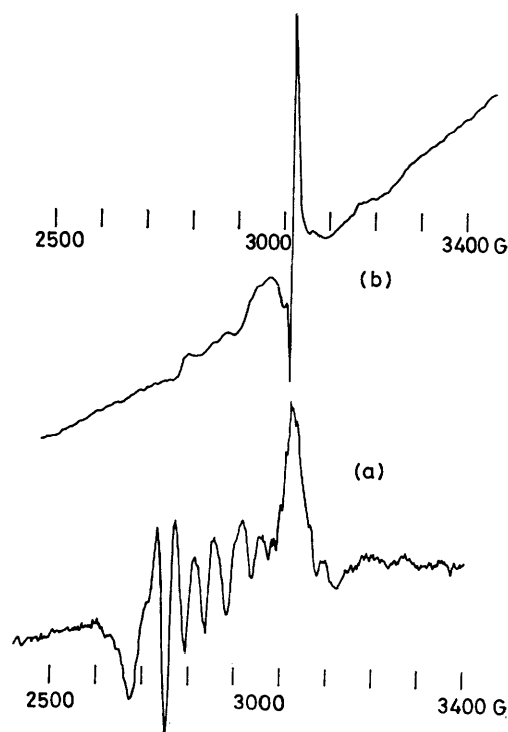


FIGURE. X-band e.s.r. spectra of manganese phthalocyanine in poly(2-methyl-1-vinylimidazole) (1%)-*NN*-dimethylformamide at 77 K: (a) without O₂ (9.23 GHz); (b) with O₂ (9.21 GHz).

(a). The complex peak structures are partly due to the nuclear spin of Mn (5/2) and also suggest the existence of more than one chemical environment for manganese. In the presence of O₂, the complex features disappeared and a

strong peak centred at $g = 2.0015$ was observed (Figure b). This change is attributed to the formation of O_2^- following transfer of one electron from Mn^{2+} , resulting in the formation of undetectable Mn^{3+} .⁴ The absence of hyperfine structure due to Mn^5 indicates negligible spin density on the Mn atom. Typical O_2^- complexes show e.s.r. absorption around $g_{||} = 2.01-2.1$ as well as a strong g_{\perp} peak around g_e (2.0023).⁴ However, the absorption due to $g_{||}$ is usually broad and its apparent intensity is very weak compared with g_{\perp} . Unfortunately in the spectrum obtained (Figure b), the

identification of the $g_{||}$ component is obscured by the presence of weak peaks presumably due to unchanged Mn^{2+} . Because of the apparent absence of any effect of PMVIm on the electronic spectrum of the complex, we assume that the complex has the composition (DMF) $\cdot Mn^{3+}\cdot Pc\cdot O_2^-$.

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