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A Manganese Phthalocyanine–Dioxygen Molecular Adduct

Sir:

In 1959, Elvidge and Lever[1] reported the ability of manganese(II) phthalocyanine (1) to bind molecular oxygen in pyridine solution, finally to yield[2] μ-oxo-bis(pyridinemanganese(III) phthalocyanine) (2) (L = pyridine) whose formation proceeds through an intermediate proposed[1] to be an oxygen adduct. Calvin and co-workers[3,4] subsequently proposed that the intermediate is $(HO)Mn^{III}Pc$ (3).[5] Clarification of this system is of considerable importance because of relevance to the role played by manganese in photosynthesis[6] and in certain dismutases.[7] The adduct[8] is now shown to be $(O_2)MnPc$ (4), as independently proposed by Uchida and co-workers,[9] who, however, presented little supporting evidence.

Oxygenation proceeds more readily in N,N-dimethylacetamide (DMA) because of a weaker manganese solvent interaction. Reaction of oxygen with $Mn^{II}Pc$ (1) in spectroquality DMA affords the sparingly soluble adduct 4 which precipitates from solution.[10] The infrared spectrum of 4 was recorded after preparation from both $^{16}O_2$ and $^{18}O_2$. Figure 1 illustrates the region near $1100\ cm^{-1}$ where an additional band at $1094\ cm^{-1}$ in the oxygen-18 spectrum appears to correspond with a pronounced shoulder in the oxygen-16 spectrum at $\sim 1154\ cm^{-1}$. These bands may be tentatively assigned as the ν(O-O)
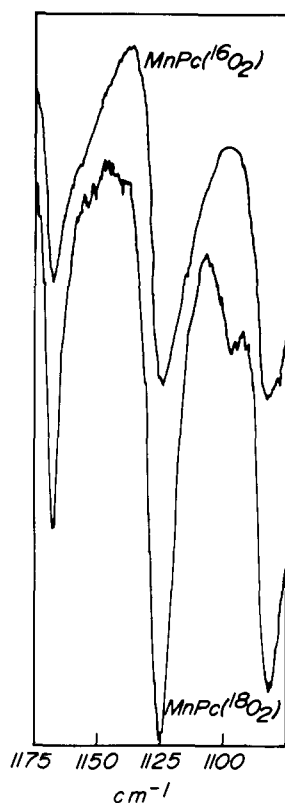
stretching vibrations of a coordinated *terminal* superoxide ion.[11] Bridging superoxides do not absorb in this region in the infrared.[12] No absorption near 800–$950\ cm^{-1}$ attributable to coordinated peroxide could be identified in these spectra.

The solid (4) is paramagnetic, the magnetic moment declining from $\sim 3.9\ \mu_B$ at 300 K to $\sim 2.6\ \mu_B$ at 84 K. In frozen DMA solution the adduct 4 exhibits a complex X-band, ~ 18-line, ESR spectrum[13] distinct from that of the other species involved. The frozen solution Q-band spectrum shows two species, a free manganese impurity and the oxygen adduct. A seven-line multiplet may be shown to correspond exactly
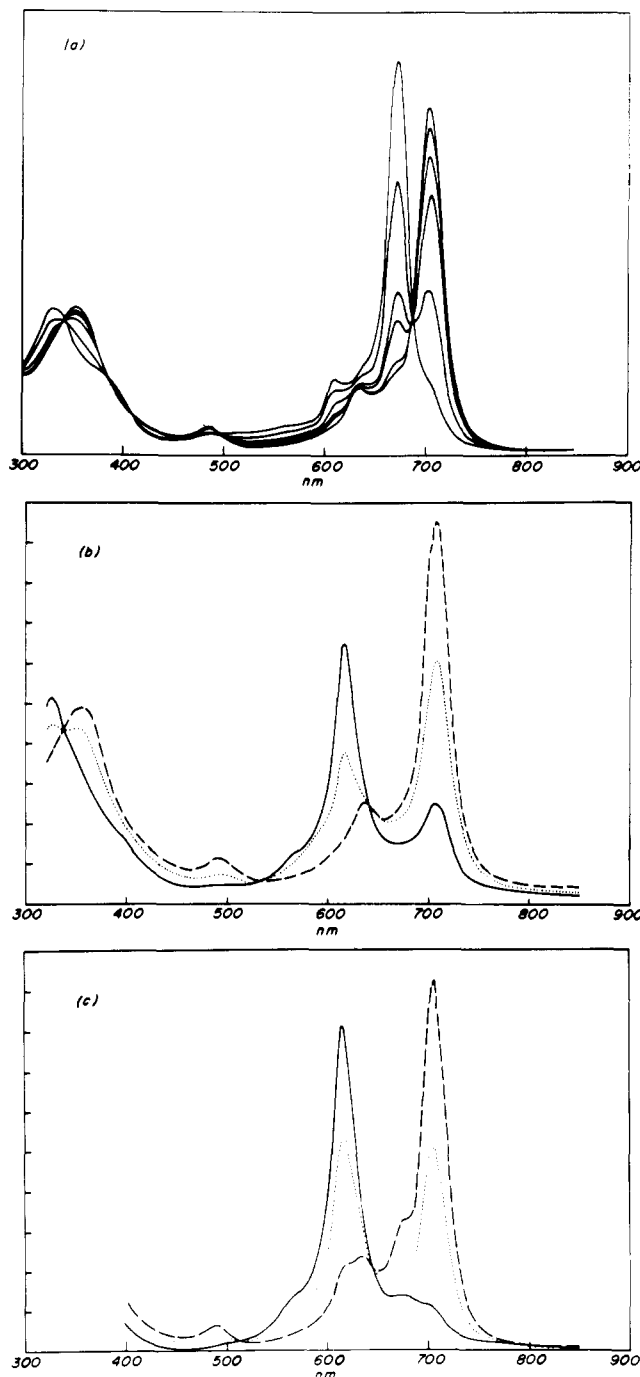

Figure 1. The infrared spectra of $(O_2)MnPc$ incorporating oxygen-16 and oxygen-18 in the region 1075–$1175\ cm^{-1}$ (Nujol mull).

Figure 2. Solution spectra in DMA at $\sim 5 \times 10^{-4}$ M concentration: (a) equilibrium conversion of PcMn(II) (λ_{max} 674) into PcMn(O_2) under various oxygen pressure; (b) conversion of pure PcMn(O_2) into (DMA)-PcMn-O-MnPc(DMA) using imidazole ($\sim 10^{-3}$ M) at $t = 0$ (- - -), $t = 3$ h ($\cdots$), and $t = 20$ h (--) (the reaction had not gone to completion under these conditions); (c) conversion of (DMA)PcMn-O-MnPc(DMA) into PcMn(O_2) with oxygen (1 atm) at $t = 0$ (—), $t = 50$ min ($\cdots$), $t = 12$ h (- - -).

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Scheme I[a]
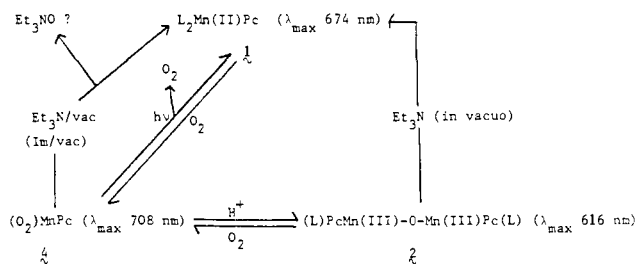
[a] L represents a solvent molecule, triethylamine or imidazole as appropriate. The absorption band maxima refer to pure DMA and may vary slightly in other solvents or when other ligands are present. The products in these reaction routes, initially identified through spectrophotometry, were confirmed by ESR and/or chemical reactivity.

(centered $\langle g \rangle$ value = 1.997, and $|A_{Mn}| = 95$ G) with a set of lines in the X-band spectrum, and provides evidence for a mononuclear manganese derivative.[14]

The visible spectra of the three major species, **1, 2,** and **4** (Figure 2), vary only slightly with change of solvent or axial ligand and their solution chemistry is therefore most readily followed spectrophotometrically in $\sim 5 \times 10^{-4}$ M solution. In this fashion the chemistry outlined in Scheme 1 was deduced.

The oxygen adduct is extremely stable. Spectroscopic monitoring shows that a solution of $Mn^{II}Pc$ is converted essentially quantitatively and in a matter of minutes into the adduct under a partial pressure of oxygen of a few Torr. A plot of $\log |(A - A_0)/(A_\infty - A)|$ vs. $P(O_2)$ monitoring the major peaks of **1** and **4** yielded a slope of unity indicating[15] formation of the 1:1 complex $(O_2)MnPc$ in solution and yielding a value of $P(O_2)_{1/2} \simeq 0.2$ Torr at 24 °C. The adduct solution is stable in vacuo at 50 °C for some hours, showing only very slow reversal. However dimethylamine, a contaminant of DMA must be absent. In the presence of species such as Me_2NH, Et_3N, and imidazole, in vacuo, the adduct is rapidly reconverted into $Mn^{II}Pc$. The adduct in vacuo also reverses to **1** in sunlight or when flashed with visible light. A suspension of **4** in DMA exposed to sunlight for several hours in vacuo releases oxygen gas as detected by mass spectroscopy. Appropriate "blanks" using a suspension of **1** showed no oxygen release. However, when a suspension of **4** in vacuo was reconverted into **1** with imidazole or triethylamine, no oxygen gas could be detected by mass spectroscopy. This appears to be another example of oxidase activity[16] for this species. The organic products have not yet been identified.

Addition of imidazole to the adduct dissolved in aerated DMA generates the μ-oxo species **2** (L = DMA) (Figure 2b). This reaction is regarded as a proton-activated decomposition of superoxide and may proceed through a dismutase-like pathway. Most significantly the μ-oxo species **2** (L = DMA) may also be converted back into the adduct **4**, under pressure of oxygen (slow, hours at 298 K) in the absence of protons (Figure 2c). Moreover, when the oxo species **2** (L = DMA) is treated with triethylamine (but not imidazole) in vacuo, it is reconverted into **1**. These reactions may be explicable in terms of a mechanism which is the reverse of the pathway proposed[17,18] for the conversion of $(TPP)Fe^{II}$ into $(TPP)Fe^{III}-O-Fe^{III}(TPP)$.

Since the solution spectrum is very similar to those of typical manganese(III) phthalocyanine mononuclear species,[3] and the infrared spectrum establishes the superoxide ion,[11,19] the most probable formulation of this adduct **4** would be $PcMn^{III}(O_2^-)$, with a moderately ionic bond. Such a species would be similar to $Zn(TPP)(O_2^-)$ except that coupling between the metal and oxygen electrons is anticipated.[20-23] The

temperature dependence of the magnetic moment is consistent with partial spin coupling between metal and superoxide, but may also be complicated by intermolecular interactions. Unfortunately solubility restrictions preclude a solution measurement of the magnetic moment.

This adduct differs from the analogue with tetraphenylporphyrin, $(O_2)Mn^{IV}(TPP)$, regarded as a peroxo species of Mn^{IV} presumably with side-bound oxygen.[24] The phthalocyanine system, which is thermally very much more stable than the TPP system, presumably contains end-on bound oxygen. The ability of manganese to bind both reduced forms of oxygen so readily may provide a clue to the mechanism of action of manganese dismutases.[7]

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