Inorg. Chem. **1981**, *20*, 761-768

ESR signal was consistent with infrared data, so it seems reasonable to conclude that the paramagnetic complex with a ν_{CO} of 2000 cm^{-1} is indeed the green cation $[Fe(CO)_3(PPh_3)_2]^+$.

An ESR spectrum of a product of chemical oxidation has previously been reported,[13] but no comment on instability of the product was made. More recent work[17] indicates a silver complex is formed as an intermediate in this reaction. This complex in turn generates the cation with release of metallic silver, and ESR spectra of even $AsPh_3$ complexes can be observed via the silver-stabilized cation despite the observation of an irreversible electrochemical response. Thus, silver complexes analogous to those proposed for mercury in this work also provide stabilized intermediates, lending strong support to the hypotheses proposed in this work.

(iii) Reaction with Acetonitrile. After generation of green $[Fe(CO)_3(PPh_3)_2]^+$ in dichloromethane via oxidation of $Fe(CO)_3(PPh_3)_2$ with silver perchlorate, acetonitrile was added dropwise. Immediately the acetonitrile was added, rapid evolution of carbon monoxide was observed, the green color faded, and infrared monitoring demonstrated the formation of $Fe(CO)_4PPh_3$. That is, the decomposition pathway for the cation appears to be catalyzed rapidly by acetonitrile. Presumably, a mechanism of the kind

$$2[Fe(CO)_3(PPh_3)_2]^+ + 2CH_3CN \rightarrow 2[Fe(CO)_2(PPh_3)_2CH_3CN]^+ + 2CO \quad (9)$$

$$2[Fe(CO)_2(PPh_3)_2CH_3CN]^+ \rightarrow Fe(CO)_4PPh_3 + Fe(II) + PPh_3 + 2CH_3CN \quad (10)$$

accounts for the decomposition of $[Fe(CO)_3(PPh_3)_2]^+$. Similar mechanisms can be proposed for all $Fe(CO)_xL_{5-x}$ species. Thus, when adsorption or complex formation at the surface occurs at mercury electrodes, this inhibits attack of the cation by a coordinating solvent, giving rise to the observation of an apparently mercury-stabilized cation. In principle, any coordinating species including acetonitrile can contribute to the decomposition of the 17-electron cation, so that the rather nonreproducible behavior noted at platinum electrodes vs. the very reproducible response at mercury is probably explicable in terms of trace, but variable amounts of coordinating impurities present in the solvent/supporting electrolyte. Alternatively, trace levels of impurity on the platinum electrode could lead to nonreproducible behavior.

Registry No. $Fe(CO)_4PPh_3$, 35679-07-3; $Fe(CO)_4AsPh_3$, 35644-25-8; $Fe(CO)_4SbPh_3$, 35917-16-9; $Fe(CO)_3(PPh_3)_2$, 21255-52-7; $Fe(CO)_3(AsPh_3)_2$, 20516-72-7; $Fe(CO)_3(SbPh_3)_2$, 20516-73-8; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8.

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Oxidation of Manganese(II) Phthalocyanine by Molecular Oxygen

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Manganese(II) phthalocyanine fails to react with oxygen when dissolved in rigorously purified, dry pyridine. Reaction does occur, however, in pure *N,N*-dimethylacetamide to yield a solution of an oxygen adduct. The reaction may be reversed slowly by degassing, more rapidly upon exposure to bright white light or upon addition of an electron donor in vacuo. Addition of certain electron donors, in oxygen, causes conversion to the known $PcMn^{III}–O–Mn^{III}Pc$. This oxy-bridged species may be reconverted to the oxygen adduct by reaction with oxygen. The oxygen adduct may be isolated as a solid. Analysis, thermodynamic measurements, infrared (oxygen-18 isotopic substitution) and electronic spectra, magnetism ($S = {}^3/_2$), and ESR appear consistent with the formulation $(O_2)Mn^{III}Pc$, a bound superoxide.

Introduction

Manganese(II) phthalocyanine when dissolved in pyridine was shown in 1959 to bind molecular oxygen reversibly,[1] to yield a product subsequently demonstrated[2] to be μ-oxo-bis((pyridine)(phthalocyaninato)manganese(III)). Despite intensive effort[3] many facets of this reaction remained to be explained. Until very recently this was the only manganese-containing system which appeared to bind molecular oxygen reversibly. Basolo, Hoffman, and co-workers[4] have now shown that MnTPP (TPP = tetraphenylporphyrin) will bind oxygen reversibly but in a fashion which seems quite different from that of the phthalocyanine. There is evidence that salen,[5a] catechol,[5b] sorbitol,[5c] and some tertiary phosphine[5d] manganese derivatives will form oxygen adducts. We might also include the rather esoteric $(O_2)Mn(CO)_5$.[6] Manganese is known to be intimately involved in the photooxidation of water during photosynthesis.[7] Studies of the binding of molecular oxygen to manganese may provide insight into the mechanism by which water bound to manganese is oxidized to molecular oxygen—hence the importance of this area of research.[8]

In this paper we describe further details of the reaction in pyridine and extend the study to solutions in *N,N*-dimethylacetamide, a more attractive solvent for this reaction. Evidence

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is presented for the oxygen adduct superoxy manganese(III) phthalocyanine.[9]

Experimental Section

Chemicals. (Phthalocyaninato)manganese(II) [PcMn^{II}] was prepared by standard methods, described previously.[10] The crude product was purified by sublimation in vacuo a minimum of three times before use. μ-oxo-bis((phthalocyaninato)manganese(III)), referred to henceforth as the μ-oxo species, was prepared according to the literature.[3,11] Pyridine (Fisher, reagent grade) was refluxed over BaO for 24 h and then distilled. The middle 80% of the distillate was again refluxed for 24 h over BaO and distilled. The middle 80% was again collected. This distillate was degassed repeatedly by the freeze–evacuate–thaw technique and then distilled while still under vacuum into the appropriate apparatus. *N,N*-Dimethylacetamide (DMA) (Aldrich Gold Label or MCB Spectroquality) was placed on the vacuum line, initially degassed at room temperature to remove dimethylamine contaminant, and then distilled onto molecular sieves (BDH type 3A), the initial 10% of solvent being rejected. The solvent was then vacuum transferred off the sieves into the reaction vessel. The sieves could be regenerated by heating with a Bunsen burner while being evacuated. Imidazole (Eastman) was recrystallized from acetone. *N*-Methylimidazole (Eastman) was purified by vacuum distillation twice from KOH. The middle 50% of the distillate was used.

Magnetic Measurements. These were recorded with a fully automatic Faraday balance of published design.[12]

Electron spin resonance measurements were obtained with a 12-in. magnet E-line Varian spectrometer, calibrated with DPPH, and a frequency meter.

Electronic spectra were recorded on a Perkin-Elmer Hitachi Model 340 spectrometer.

Infrared spectra were recorded on a Beckman Model IR-12.

Mass spectra were obtained with a Perkin-Elmer RMU 6 single-focusing mass spectrometer.

Spectrophotometric Measurements. One-hundred-milliliter bulbs, equipped with a side arm on which was attached a quartz cell (1.00- or 0.1-cm path length), were used as the reaction flasks. These flasks, furnished with a 7-mm O-ring joint and a Teflon vacuum stopcock (Kontes, Vacuum Teflon Valve, No. K-826600), were connected to a vacuum manifold capable of maintaining a low pressure of 10^{-5} mm for several days without leakage. Attached to the manifold were a mercury manometer, a drying train for gases, and four outlets equipped with Teflon vacuum stopcocks and 7-mm O-ring joints to allow the attachment of flasks. Several one-necked flasks with 7-mm O-ring joints were also used for the storage of solvents on the manifold.

So that the reactivity of a (phthalocyaninato)manganese(II) solution with oxygen could be determined, 25 mL of the solvent to be studied was placed on a 100-mL flask and connected to the manifold. The solvent was degassed a minimum of four times by the freeze–evacuate–thaw method. The degassed solvent was then stored under vacuum on the manifold. A small quantity (50–100 μg) of pure, triply sublimed manganese(II) phthalocyanine was placed in the reaction flask, along with a magnetic micro stirring bar. The flask was then connected to the vacuum manifold and evacuated. The flask and its contents were flame-dried while the flask was being evacuated. The solvent flask was then opened to the manifold and the solvent "trap-distilled" into the reaction vessel. The solution was stirred vigorously until homogeneous. The flask was then disconnected from the manifold and the visible spectrum of the solution obtained by tipping the solution into the cuvette on the side arm. After the spectrum was obtained, the solution was poured back into the main flask and the reaction vessel was reconnected to the vacuum manifold. The manifold was reevacuated and then closed off from the pump. Oxygen (or air) was allowed to enter the manifold via the drying train, and the gas pressure was monitored with the manometer. Once the desired pressure was attained, the gas flow was stopped and the reaction flask was opened to the manifold. After 30 s of stirring, the flask was resealed and removed from the manifold. The spectrum of the oxygenated solution was then monitored in the cuvette for up to 24 h.

Equilibrium Constant Measurements. In a typical measurement the MnPc was placed in the reaction flask, and dry DMA was trap-distilled into the vessel, following the above procedures (final concentration approximately 10^{-4}–10^{-5} M). The flask was then placed in a thermostated bath (precision Scientific Lo-Temptrol) at 23.0 ± 0.1 C. The basic experiment involves the exposure of the PcMn^{II}/DMA species to various pressures of oxygen and monitoring of the equilibrium spectrum. Experience revealed that unless the glassware and solvent were scrupulously clean, the presence of adventitious electron donors would convert some of the oxygen adduct to the μ-oxo species. This reveals itself by growth of a band at 620 nm. Such experiments were rejected. Indeed the experiment was repeated many times to generate a series of runs in which PcMn^{II} is cleanly converted into the oxygen adduct, as indicated by the clean conversion of the band at 674 nm (PcMn^{II}) to 705 nm (PcMn(O$_2$)) with no significant growth in the 620-nm band. It was found useful to trap-distill some anhydrous triethylamine into the reaction vessel prior to the experiment. This had the value of reducing any traces of adduct or other PcMn^{III} species which might be present. Indeed it is possible to begin the reaction with a pure PcMn^{III}X, e.g., X = OAc, species and reduce it in vacuo with triethylamine prior to undertaking the oxygenation study. Since triethylamine slows the rate of oxygenation, it must be removed by pumping on the sample at room temperature until the manifold indicates a solvent pressure of about 0.05 torr.

The spectrum of the initial PcMn^{II}/DMA species is recorded from 300 to 850 nm. Low oxygen pressures are introduced by admitting air through a drying train into the manifold. Air pressures of between 5 and 25 mm (oxygen from 1 to 5 mm) were employed for the initial data, and a pressure close to an atmosphere of oxygen was used to obtain the limiting adduct spectrum. The spectrum was recorded after about 15 min, even though the reaction is almost complete in the time of mixing. The changes in spectrum as a function of oxygen pressure were specifically monitored at 705 nm (growth in intensity due to growth of adduct), 674 nm (decrease in intensity due to loss of PcMn^{II}), and 332 nm (decrease in intensity due to loss of PcMn^{II}). We use the equation[13]

$$\log\,[(A - A_0)/(A_\infty - A)] = \log K + n \log P_{O_2} \qquad (1)$$

where K is the equilibrium constant for the reaction

$$\text{PcMn}^{II} + n\text{O}_2 \rightarrow \text{PcMn(O}_2)_n \qquad (2)$$

A is the absorbance at a specific oxygen pressure and A_0 and A_∞ are the initial and limiting absorbances at zero and high oxygen pressures, respectively. The slope of eq 1 provides n, the number of oxygen molecules bound to manganese, and the intercept on the log (pressure) axis provides log K. The pressure at which the PcMn^{II} is half-oxygenated, $P_{1/2}$, is given by antilog (−log K). In a typical run we observed

wavelength, nm	332	674	705
log K	0.77	0.82	0.62
$P_{1/2}$, mm	0.17	0.15	0.24
slope (n)	0.97	0.81	1.04

Over five successful runs the slope (standard deviation) was 1.01 (0.01) and $P_{1/2}$ was 0.20 (0.019) mm. Higher values of $P_{1/2}$ were obtained if some triethylamine remained in the reaction mixture.

Manganese(II) Phthalocyanine–Dioxygen Adduct. The manganese phthalocyanine oxygen complex was prepared in a modified Schlenk apparatus consisting of two 100-mL flasks, connected by a porcelain frit of medium porosity, to facilitate the filtering of solutions under nitrogen. Dry DMA (30 mL) and a magnetic stirring bar were placed in one flask, the solvent was degassed for 35 min with dry nitrogen ("High Purity", Linde), and then freshly sublimed (phthalocyaninato)manganese(II) (50 mg, 8.8 × 10^{-5} mol) was added. After 30 min of stirring under nitrogen, the resulting solution was filtered through the frit. The filtrate was then exposed to oxygen overnight, whereupon a greenish black solid precipitated. Anhydrous ether (20 mL) was added to the mixture to enhance precipitation. The resulting mixture was centrifuged, and the precipitate was washed and re-

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centrifuged several times in anhydrous ether. The material was then dried in vacuo over $CaSO_4$ (anhydrous) at room temperature. The reaction was performed several times, with a typical yield being 25 mg or 47%. The poor yield was due principally to the loss of material in the initial filtrations. Anal. Calcd for $C_{32}H_{16}MnN_8O_2$: C, 64.1; H, 2.7; Mn, 9.2; N, 18.7. Found: C, 64.1; H, 3.3; Mn, 9.1; N, 18.3.

Electronic spectrum in DMA, λ_{max} in nm (log ϵ): 295 (3.90), 355 (4.02), 417 (3.94), 495 (3.74), 634 (3.98), 678 sh, 705 (4.63) (concentration was 4.24×10^{-5} M).

Solid samples of the oxygen complex were also prepared from $^{18}O_2$ (very kindly supplied by Professor R. R. Gagne, California Institute of Technology). The sample was prepared on a vacuum manifold, whereby dry, degassed DMA (10 mL) was trap-distilled onto a sample of MnPc (50 mg) in a 50-mL flask. The resulting solution was then exposed to 600 mm of $^{18}O_2$ for 1 h. The excess $^{18}O_2$ was then recovered, and the resulting sample was worked up in the standard fashion. Infrared spectra were obtained for samples of the complex prepared from $^{16}O_2$ and $^{18}O_2$ (vide infra).

Magnetic measurements[12] were obtained with a number of adduct samples. Values ranging between 3.70 and 3.95 μ_B at room temperature were observed. A typical data set follows [temp (K), corrected $\chi_M \times 10^6$ (cgsu) (diamagnetic correction 447×10^{-6} cgs), μ_{eff} (μ_B)]: 84.0, 9926, 2.58; 90.3, 9587, 2.63; 95.9, 8834, 2.60; 106.5, 8677, 2.72; 114.9, 8446, 2.78; 119.6, 8268, 2.81; 125.9, 8091, 2.855; 138.6, 8384, 3.05; 151.0, 8048, 3.12; 164.7, 7748, 3.195; 182.1, 7449, 3.29; 196.6, 7257, 3.38; 211.0, 7029, 3.445; 242.1, 6664, 3.59; 258.0, 6545, 3.68; 284.2, 6286, 3.78; 302.5, 6383, 3.93; 305.7, 6295, 3.92.

Electron Spin Resonance Studies. X-Band spectra and Q-band spectra of the adduct (courtesy of Professor D. Chasteen, University of New Hampshire) were obtained by suspending a sample of Mn(II), or better (because of greater solubility) $PcMn^{III}–O–Mn^{III}Pc$, in pure solvent (usually DMA) and oxygenating for about 30 min with pure, dry oxygen. Aliquots of these solutions were frozen and their spectra recorded. Since $PcMn(O_2)$ is not very soluble in DMA, prolonged reaction under these conditions leads to precipitation and poor-quality ESR spectra. The Q-band spectrum and the X-band spectrum were recorded in different tubes (because of relative cavity size) with use of the same bulk solution of the adduct. The X-band spectrum was recorded subsequent to the Q-band spectrum, ensuring that no decomposition had taken place.

Hydroxo(phthalocyaninato)manganese(III). (Phthalocyaninato)manganese(II) (0.20 g, 3.5×10^{-4} mol) was dissolved in pyridine (50 mL), and air was bubbled through the resulting solution until it was determined spectroscopically to be μ-oxo-bis((pyridine)(phthalocyaninato)manganese(III)).[11] The solution was then filtered, and water (approximately 0.25 mL) was added. The resulting mixture was stirred for 3 days under nitrogen, until its visible spectrum had changed completely from λ_{max} 620 nm (μ-oxo species) to λ_{max} 717 nm, characteristic of a (phthalocyaninato)manganese(III) monomer. The species was isolated from solution by the addition of ether (approximately 25 mL), whereupon a greenish blue precipitate formed. This was collected by centrifugation, washed several times with ether, and dried over $CaSO_4$ in vacuo.

The formation of the above complex was also affected in *N,N*-dimethylacetamide. The same procedure was employed, and a nearly quantitative yield of a greenish black ESR-quiet solid was obtained. Anal. Calcd for $C_{32}H_{17}MnN_8O$: C, 65.8; H, 2.9; Mn, 9.4; N, 19.2. Found: C, 65.9; H, 2.8; Mn, 10.0; N, 18.4.

Some difficulty was experienced in obtaining a satisfactory analysis of this complex. The magnetic moment was 4.88 ± 0.05 μ_B at 293 K. Electronic spectrum in DMA, λ_{max} in nm (log ϵ): 359 (4.18), 503.5 (3.78), 646 (4.01), 717 (4.69).

Reaction of Imidazole with the Oxygen Adduct in Vacuo. A solution of the oxygen adduct in DMA was prepared as indicated above and placed in an ESR tube. Imidazole was also placed in a side arm of the tube. The system was degassed and the ESR spectrum monitored to confirm the presence of only the adduct. The imidazole was tilted into the adduct solution. Fairly rapid reaction (about 10 min) occurs to form (phthalocyaninato)manganese(II). This is detected by its characteristic low-spin ESR spectrum[14] ($g_\parallel = 2.00$, $g_\perp = 2.12$, $A_\parallel = 166$ G, $A_\perp = 24$ G).

A similar experiment was carried out in a cuvette and the optical spectrum of $Mn^{II}Pc$ observed. In a third experiment a suspension of $PcMn(O_2)$ was treated in vacuo, with imidazole and the system shaken for about 2 h in the dark. When the atmosphere above the solution was monitored with a mass spectrometer, no increase in the oxygen signal, above background, could be detected (see below).

Reaction of the Oxygen Adduct with Other Reagents and with Light. In a series of experiments $PcMn(O_2)$ was generated in an evacuable cuvette via reaction with $PcMn^{II}$ or PcMn–O–MnPc with oxygen, in DMA. The reaction of this species with various reagents including triethylamine, imidazole, *N*-methylimidazole, trimethylamine, catechol, water, and visible light, both in vacuo and in the presence of oxygen, were monitored via electronic spectroscopy. In most cases the spectroscopic signatures of the products provided unequivocal characterization of the reaction. In a few cases the reactions were repeated at higher concentrations and the ESR spectra recorded, according to the details given previously for imidazole. Visible light was provided via sunlight or a commercial photographic flashlamp (1-ms duration, 5800 °F color temperature). Reaction of one of the above reagents, under oxygen, was effected as follows. An oxygenated solution of the adduct was frozen, on the vacuum line, and the system evacuated, thereby leaving a frozen *oxygenated* solution under vacuo. The reagent of choice was vacuum transferred to the frozen solution. Oxygen was then reintroduced to the flask *prior* to rewarming the solution back to room temperature.

Detection of Oxygen Gas. Photochemical decomposition of $PcMn(O_2)$ with sunlight yields $PcMn^{II}$ and molecular oxygen. The former was detected via its electronic spectrum; the latter, by mass spectroscopy, as follows.

$PcMn(O_2)$ (25 mg) was suspended in DMA (about 10 mL in a Pyrex flask containing a micro spin bar) and the system evacuated. The solution was stirred in direct sunlight for about 2 h. The flask was then connected to a mass spectrometer and the signals at *m/e* 32 (oxygen) and *m/e* 28 (nitrogen) recorded. In duplicate experiments both the absolute signal intensity at *m/e* 32 and the *ratio* of the signals at 32 and 28 increased relative to background, providing direct evidence for an increase in oxygen which could not have arisen from an atmospheric leak. When the experiment was repeated with $PcMn^{II}$, no increase in signal *m/e* 32 was observed. Moreover when a similar experiment was carried out with $PcMn(O_2)$ and triethylamine or imidazole instead of sunlight, reduction occurs to $PcMn^{II}$ but no oxygen was detected. In both the sunlight and triethylamine reactions, the product, after reaction, was shown to contain $PcMn^{II}$, via ESR spectroscopy.

Results and Discussion

At the initiation of our renewed investigation into the manganese phthalocyanine/oxygen problem, the following facts had been deduced by earlier studies.

(i) Manganese phthalocyanine is soluble in pyridine to form a blue-green solution of the low-spin six-coordinate[14] $(py)_2Mn^{II}Pc$.

(ii) This solution absorbs oxygen, ultimately to form $[(pyMn^{III}Pc)_2O]$, a presumed six-coordinate, diamagnetic,[11] oxidation product, the μ-oxo species (λ_{max} 620 nm).

This deep blue solution returns to the Mn(II) oxidation level by prolonged degassing with nitrogen (half-life a few days at room temperature and faster at elevated temperatures).

(iii) During the progress of the oxidation in pyridine, an intermediate is formed, absorbing near 710 nm. This absorption band grows in intensity during the initial oxidation process, shifting in frequency slightly during this process, suggesting the presence of two intermediates, and then decays to zero with the continued growth of the μ-oxo species.[3] Absorption near 710 nm is characteristic of a monomeric manganese(III) phthalocyanine.[3]

There is evidence that all three species, $(py)_2Mn^{II}Pc$, intermediate, and μ-oxo species, are in equilibrium with each other and presumably with oxygen and that the rate of the oxygenation is influenced by traces of water vapor. The presence or absence of light also influences the position of this equilibrium.[3]

(iv) Addition of acid to the μ-oxo species solution causes a color change to grass green and the formation of a monomeric Mn(III) species typified by absorption near 710 nm;

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(14) Phillips, L. K. Ph.D. Thesis, University of California, Berkeley, CA, 1967.

i.e., the bridge is cleaved by excess protons.[15] In the original communication, Elvidge and Lever,[1] on the basis of the sparse evidence available at that time, postulated the presence of a peroxy-bridged binuclear manganese(III) intermediate. Calvin and co-workers[3] preferred the monomeric hydroxy species ($HOMn^{III}Pc$) as the intermediate. Evidence is provided here that the intermediate is in fact a 1:1 oxygen adduct.

Further Studies with the $Mn^{II}Pc$/Pyridine System. Since the various species in this system have quite different electronic spectra (see Figure 2 in ref 9), it is most convenient to follow the reactions spectrophotometrically. Solutions of appropriate concentration are made up on a vacuum line by vacuum transfer of pure degassed reagent into a vessel containing manganese(II) phthalocyanine. With appropriate care the solutions so produced exhibit bands at 880, 660, and 467 nm, indicative of a solution of $Mn^{II}Pc$ in pyridine; lack of absorption bands at 620 and 710 nm illustrates the absence of the μ-oxo species and of monomeric Mn(III) species, respectively. Using this technique coupled with ESR spectroscopy, it is possible to make the following observations.

(i) Reaction, with the formation of the intermediate and subsequent formation of the μ-oxo species, is inhibited if the pyridine is rigorously dried and purified. Such a solution of $Mn^{II}Pc$ in pyridine when contacted with dry oxygen shows only a very slow reaction over a period of days. This latter reaction probably occurs through very slow leakage of moist air into the system. In the presence of trace amounts of water this reaction is usually essentially complete within $^1/_2$ h.

(ii) If, under dry conditions, a crystal of imidazole is admitted to the vessel in (i) above, reaction to the μ-oxo species is complete within 20 min. The ESR spectrum of $Mn^{II}Pc$ dissolved in pyridine fades as oxygenation proceeds to generate the ESR-quiet μ-oxo species. Since reaction proceeds via the intermediate, it appears that formation of the μ-oxo species provides the driving force to shift the equilibrium in favor of the oxygen adduct.

If imidazole is added to a degassed sample containing all three species ($Mn^{II}Pc$, intermediate, and μ-oxo species), the ESR signal arising from Mn(II) *increases* in intensity. Closer examination reveals that imidazole, in the absence of oxygen, will reverse the intermediate back to $Mn^{II}Pc$.

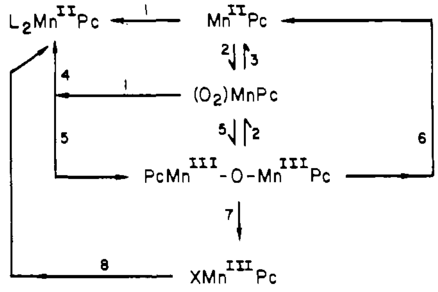
(iii) The hydroxy species $HOMn^{III}Pc$ was isolated (see Experimental Section) and dissolved in pyridine. A green solution whose absorption spectrum was characteristic for a monomeric $Mn^{III}Pc$ species was obtained and was found to be insensitive to moist air. This experiment appears to preclude the hydroxy species as the intermediate as claimed by Calvin.[3] Moreover this species absorbs at a significantly higher wavelength than the intermediate (717 nm rather than 708 nm). Detailed electrochemical studies have been carried out on the $Mn^{II}Pc$/py system.[16]

The following observations are relevant to the oxygenation problem.

(a) Electrochemical oxidation of $Mn^{II}Pc$ in pyridine leads to a monomeric $Mn^{III}Pc$ derivative which does not absorb oxygen nor give rise to the μ-oxo species in pyridine. In DMA/Et_4NClO_4 this species is $(ClO_4)Mn^{III}Pc$.[16]

(b) The blue oxygenated solution contains manganese at the +3 oxidation level. Both solid $(pyMn^{III}Pc)_2O$ and the oxygenated solution in pyridine exhibit strong absorption at 620 nm. There seems to be little doubt from these observations that the μ-oxo species identified by X-ray studies is identical with the fully oxidized species in pyridine solution. The original premise that the oxygenated solution contains a Mn(IV) species[1,3] is now definitely excluded. We may view the reaction in pyridine as replacement of one of the pyridine ligands coordinated to manganese(II) by oxygen to yield an intermediate which is not the hydroxymanganese(III) species and presumably parallels the products in DMA (see below). Proof for this postulate will be very difficult to obtain because of the transient nature of this species in pyridine. It seems reasonable to suppose that reaction to the intermediate might be more favored in a less strongly donating solvent.

Scheme I[a]



[a] Key: 1, ligands such as imidazole or triethylamine; 2, oxygen in pure DMA; 3, nitrogen degassing (slow)—more rapid on heating or exposure to visible light or upon addition of imidazole; 4, addition of imidazole under anerobic conditions; 5, addition of imidazole in presence of air or oxygen; 6, vacuum or nitrogen degassing of DMA solution, facilitated by visible light; 7, excess X^-, where $X^- = Cl^-$, OH^-, or HX for most X; 8, for example, for $X = OAc^-$, Et_3N in vacuo.

The Manganese(II) Phthalocyanine/Dimethylacetamide (DMA) System. Reaction of dry oxygen with a solution of $Mn^{II}Pc$ in pure DMA results in the almost instantaneous formation of a green species (see Figure 2a in ref 9), which is evidently one of the intermediates. This may be returned very slowly (half-life many days at room temperature) to the $Mn^{II}Pc$ starting material by degassing or rapidly (~10 min) by addition of imidazole or methylamine under nitrogen or by flashing with visible light (see Figure 2b in ref 9). Addition of imidazole and oxygen results in the rapid formation of the blue μ-oxo species (see Figure 2b in ref 9 and Scheme I). Thus the system is analogous to the pyridine system except that DMA is coordinated weakly enough to the manganese to permit replacement by oxygen directly.

Indeed the green solution of the intermediate is sufficiently stable to enable isolation of the solid now formulated[9] as $PcMn(O_2)$. The growth of the 708-nm band may be monitored as a function of oxygen pressure; a plot[13,17] of log $[(A - A_0)/(A_\infty - A)]$ vs. log P_{O_2} yielded a slope of unity and a K for reaction 3 of 0.7 mm^{-1}. The slope of unity infers the presence of a 1:1 $PcMn^{II}/O_2$ adduct.

$$PcMn^{II} + O_2 \rightleftharpoons PcMn(O_2) \qquad (3)$$

Thus $P_{1/2}$, the pressure of oxygen necessary to convert half of the $PcMn^{II}$ species to product is close to 0.2 mm. Evidently, $PcMn^{II}$ has a greater affinity for oxygen than do cobalt porphyrins[17] and iron porphyrins.[18]

In pure DMA the reaction is rapid, being essentially complete in the time of mixing. On the other hand, if the reaction is carried out in DMA in the presence of significant amounts of dry triethylamine, the reaction is slowed down and can now take hours to reach completion. This is consistent with the initial displacement of a coordinated triethylamine molecule by an incoming oxygen molecule. The formation of the adduct is truly reversible in that, when exposed to sunlight in vacuo, the adduct regenerates $PcMn^{II}$ and molecular oxygen detected

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by mass spectrometry (see Experimental Section). However, when the adduct is reconverted to $PcMn^{II}$ with reagents such as imidazole, triethylamine, catechol, etc., in vacuo,, no oxygen appears to be released. Presumably the adduct is demonstrating oxidase activity as proposed by Uchida and coworkers.[19]

In the absence of electron-donor molecules such as those listed above, the adduct solution is resistant to outgassing by nitrogen at temperatures as high as 50 °C. In boiling solvent, however, $PcMn^{II}$ can be rapidly recovered. A solution of the adduct in DMA, which has not been adequately dried and which has stood for some hours, can be reversed rapidly at 50 °C because of the intermediate buildup of dimethylamine due to solvent hydrolysis. Thus in the absence of an electron source, a solution of the adduct is extremely stable, far more so than iron or cobalt oxygen adducts. This observation is consistent with the smaller $P_{1/2}$ determined.

Conversion of the adduct to the μ-oxo species might occur via two general pathways: (i) displacement of O_2^- by OH^- followed by dehydration of two molecules of $HOMn^{III}Pc$ or (ii) scission of the dioxygen unit with or without involvement of protons. Possibility i is excluded in that the superoxide ion is not detected by ESR spectroscopy and the electronic spectroscopic signatures of hydroxymanganese(III) phthalocyanines are not seen in the conversion of adduct to μ-oxo species. Given that conversion of the adduct to μ-oxo species takes place in rigorously dried pyridine, in the presence of imidazole, the incorporation of at least one of the superoxide oxygen atoms into the μ-oxo species seems ensured.

A solution of the adduct in DMA may be smoothly but slowly (half-life $\simeq$ $^1/_2$ h at room temperature) converted into the μ-oxo species by addition of imidazole or *N*-methylimidazole, but not by 2-methylimidazole, triethylamine, or water (small amounts of which fail to react with the adduct). We speculate that the mechanism parallels that proposed[20-22] for the conversion of $(TPP)Fe^{II}$ into $(TPP)Fe^{III}{-}O{-}Fe^{III}(TPP)$ upon oxygenation (TPP = tetraphenylporphyrin), namely eq 4–8.

$$PcMn^{II} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PcMn(O_2) \qquad (4)$$

$$PcMn(O_2) + PcMn^{II} \rightleftharpoons PcMn^{III}{-}O_2{-}Mn^{III}Pc \qquad (5)$$

$$PcMn^{III}{-}O_2{-}Mn^{III}Pc \rightleftharpoons 2PcMn^{IV}O \qquad (6)$$

$$2PcMn^{IV}O + PcMn^{II} \rightleftharpoons 2PcMn^{III}{-}O{-}Mn^{III}Pc \qquad (7)$$

$$\text{net} \quad 4PcMn^{II} + O_2 \rightarrow 2PcMn^{III}{-}O{-}Mn^{III}Pc \qquad (8)$$

In pure DMA the reaction stops at the formation of $PcMn(O_2)$ (eq 4) because $k_1 \gg k_{-1}$ and there is essentially no free $PcMn^{II}$ in solution to proceed via reaction 5. The addition of an effective reducing agent such as imidazole or *N*-methylimidazole provides some $PcMn^{II}$ for reaction to continue to completion but at a rate very much slower than k_1. The effectiveness of *N*-methylimidazole infers that protons are not strictly necessary for this reaction as had previously been assumed.[9] The failure of 2-methylimidazole to react (in a reasonable time period) may be explained on the basis that imidazole and *N*-methylimidazole react by transfer of an electron from the 2-position of the imidazole ring, a reaction which is kinetically blocked by the 2-methyl substituent.[23]

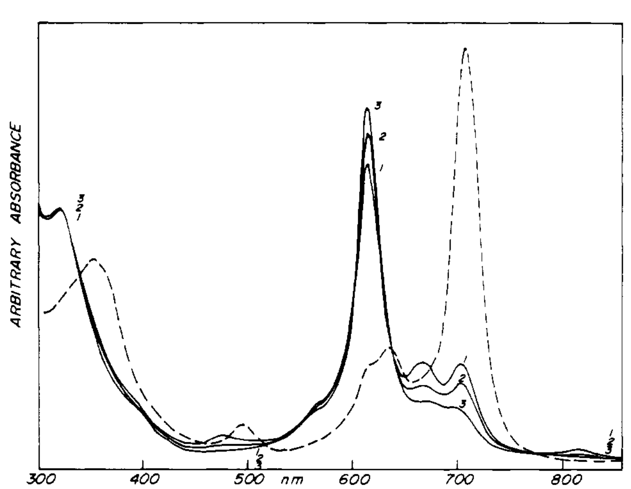

Figure 1. Reaction of *N*-methylimidazole with $PcMn(O_2)$ in DMA at room temperature, under oxygen. The hatched line displays the initial $PcMn(O_2)$ electronic spectrum. The solid lines 1, 2, and 3 display the electronic spectra approximately 4, 9, and 14 min after addition of *N*-methylimidazole. Note the existence of several isosbestic points and the presence of $PcMn^{II}(N\text{-Me-Im})_2$ as characterized by bands at approximately 475, 666, and 816 nm, which grow initially and then decay to reveal in spectrum 3 almost pure $PcMn^{III}{-}O{-}Mn^{III}Pc$ (a trace of which is revealed in the initial $PcMn(O_2)$ spectrum). The columns of numbers 1, 2, 3 reveal the order of the spectra where such is not clear.

Water fails to react because it is not a good electron donor. Close scrutiny of the spectroscopic changes involved during the conversion of the adduct to the μ-oxo species (Figure 1) indeed reveals that, even though this reaction is carried out under oxygen, a small amount of $PcMn^{II}$ is seen and remains present until all the oxygen adduct has disappeared. This is strong evidence for the intermediacy of $PcMn^{II}$. Reactions 4–8 however cannot be a complete representation of the mechanism. If equal amounts of $PcMn^{II}$ and $PcMn(O_2)$ are mixed in DMA under vacuum, there is no observable reaction over a period of hours. Evidently either oxygen or, more likely, the added reducing ligand plays a role in driving the reaction forward. Conceivably good donor ligands facilitate reaction 6.

Most significantly, if the μ-oxo species is dissolved in DMA and treated with molecular oxygen, it is smoothly converted back to the adduct (see Figure 2c in ref 9), proven not only by electronic spectroscopy but also by the generation of the characteristic ESR spectrum (see below). This completes the cycle of reactions as expressed in Scheme I. The rate of reaction is fairly slow; monitoring the loss of the 620-nm band or the growth of the 705-nm band under an atmosphere of pure oxygen yields a pseudo-first-order rate constant of 1.71×10^{-4} s^{-1} at 25 °C. Addition of imidazole to the resulting solution causes recovery of the original spectrum (energy and intensity) of the μ-oxo species, providing further characterization of the reaction. Knowledge of the mechanism of this reaction is especially important to have because of the implication of oxidation of oxide ion to molecular oxygen (see footnote 18 of ref 9) and relevance to photosynthesis.[7] Calvin had noted, and we have confirmed, that the μ-oxo species is prone to disproportionation under vacuo in the dark in wet pyridine.[3] Disproportionation does not occur in rigorously dried pyridine. Disproportionation of the μ-oxo species is facile, under vacuo, in pure DMA. From electronic spectroscopy we infer that $PcMn^{II}$ and $PcMn(O_2)$ are formed. This disproportionation reaction may occur through the reverse of sequence of (4)–(8) and provides a rationale for the conversion of the μ-oxo species back to the adduct in the presence of oxygen. However the disproportionation reaction in DMA is not very well-behaved. The relative proportions of $PcMn^{II}$ and $PcMn(O_2)$ vary from

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one experiment to another making it difficult to confirm the hypothesis above. Note that if imidazole is added to the μ-oxo species in DMA, under vacuo, disproportionation is totally suppressed, and subsequent addition of oxygen will not convert the μ-oxo species back to $PcMn(O_2)$. In consonance with this scenario, a solution of the μ-oxo species in pyridine will not react with molecular oxygen. Note also that $(TPP)Fe^{III}$–O–$Fe^{III}(TPP)$ will not react with molecular oxygen.[24]

Infrared Spectrum. Isotopic substitution with oxygen-18 led to the tentative identification of the ν(O–O) stretching vibration observed as a weak shoulder at 1154 cm^{-1} in the oxygen-16 adduct, shifting to become a very weak peak at 1096 cm^{-1} in the oxygen-18 adduct (see Figure 1 in ref 9). Such a band position and isotopic shift is fully consistent with such a vibration in a bound superoxide derivative.[25] There was no change in the 750–950-cm^{-1} region upon isotopic substitution, thereby eliminating the peroxide group bound in an infrared-active fashion. Note that when the oxygen molecule binds two equivalent metals (1:2 complex), it is not infrared active.[26] The infrared data therefore support a terminal superoxide-like dioxygen adduct. Although the infrared signature of the superoxide ion is generally sharper and more spikelike than appears here, we note that the bandwidth at half-height of the $^{18}O_2$ absorption is about 8 cm^{-1}, essentially the same as observed in hemoglobin–O_2.[27] Moreover the tetrasulfonated-phthalocyanine analogue of the oxygen adduct $(TsPc)Mn(O_2)$ has been prepared. A Raman isotopic substitution experiment shows a band at 1135 cm^{-1} in the oxygen-16 spectrum shifted to 1050 cm^{-1} in the oxygen-18 spectrum,[28] in excellent agreement with the infrared data above.

Electronic Spectrum. The electronic absorption spectrum (Experimental Section) (Figure 1) of the species, now firmly established as an oxygen adduct from the data presented above, is characteristic of a manganese(III) phthalocyanine.[3] Monomeric manganese(III) complexes exhibit intense absorption bands in the range 700–730 nm and near 355 nm (Soret) and a weaker band at about 500 nm.[3] These features are observed with the adduct. Indeed the spectrum is almost indistinguishable from that of $PcMn^{III}(OAc)$ and arises through transitions within the phthalocyanine unit perturbed by the central ion. The similarity of the acetate and oxygen adduct would imply that the appropriate electronic description of the complex would be manganese(III) with a fairly ionic superoxide ligand, perhaps rather like $Zn(TPP)(O_2^-)$.[29]

Magnetic and ESR Data. The solid adduct, whose mull transmittance spectrum is essentially the same as the solution spectrum, exhibits a room-temperature magnetic moment of ~3.9 μ_B which decreases with decreasing temperature (Experimental Section). Combination of the spin of d^4 $PcMn^{III}$ with $S = {}^1/_2$ of O_2^- may lead to spin states of $S = {}^5/_2, {}^3/_2$, or ${}^1/_2$. The observed moment could be consistent with exchange-coupled $S = {}^5/_2$ or $S = {}^3/_2$. However, all known oxygen adducts involve at least partial spin-pairing between metal and oxygen. The $S = {}^5/_2$ system therefore seems highly improbable. We prefer the $S = {}^3/_2$ possibility which is consistent with the coupling[30] observed with other metalloporphyrin dioxygen adducts, e.g., two unparied electrons for $TPPCr^{III}(O_2^-)$,[31] one for similar cobalt(III) analogues,[32] and diamagnetism for iron(III).[33] The temperature dependence may arise through further spin coupling approaching the $S = {}^1/_2$ state at lower temperature or from intermolecular coupling in the solid state. The latter is favored because the electron spin resonance spectrum in frozen solution is independent of temperature from about 4 to 220 K. Moreover the ESR spectrum is independent of solvent. Thus the complex could be construed to be five-coordinate, as are other $PcMn^{III}X$ derivaives,[34] with weak intermolecular coupling in the solid state (see MO diagram below).

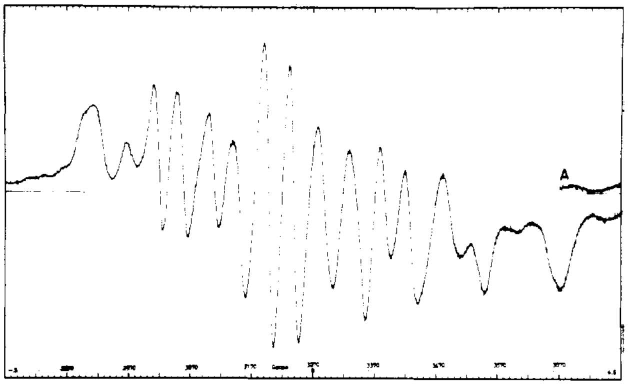

Figure 2. X-Band electron spin resonance spectrum of $PcMn(O_2)$ dissolved in *N,N*-dimethylacetamide at approximately 4 K. The signal labeled A is offset 100 G and is, therefore, a continuation of the main spectrum. Instrumental parameters: gain 8×10^3, frequency 9.153 GHz, pen response 0.032 s, power 0.5 mW, acquisition time 4 min, modulation amplitude 4 G, range 2770–3870 G.

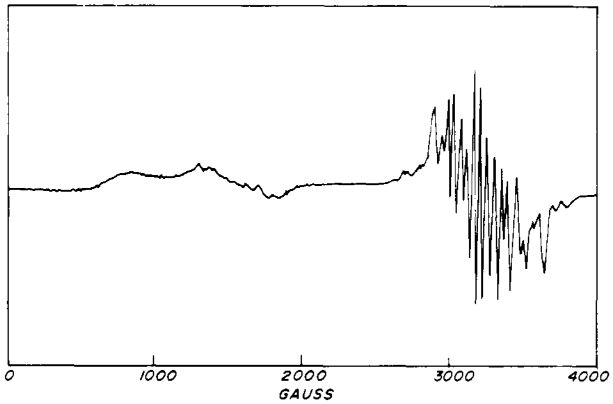

Figure 3. X-Band electron spin resonance spectrum of $PcMn(O_2)$ dissolved in *N,N*-dimethylacetamide at approximately 4 K. Instrumental parameters: gain 5×10^3, frequency 9.150 GHz, pen response 0.016 s, power 0.2 mW, acquisition time 2 min, modulation amplitude 8 G, range 0–4000 G.

The electron spin resonance spectrum of the oxygen adduct (Figure 2, X band) shows some 18 lines in low-temperature frozen solution and is quite different from that observed with $(O_2)Mn(TPP)$[4] (and different from a previously reported[35] spectrum of so-called $PcMn(O_2)$). Data were obtained at liquid-helium temperature, and a search was made for absorption at both low and high fields. There is indeed some absorption at g = 4–6 (Figure 3). However, the intensity of this absorption, relative to that centered near g = 2, varied

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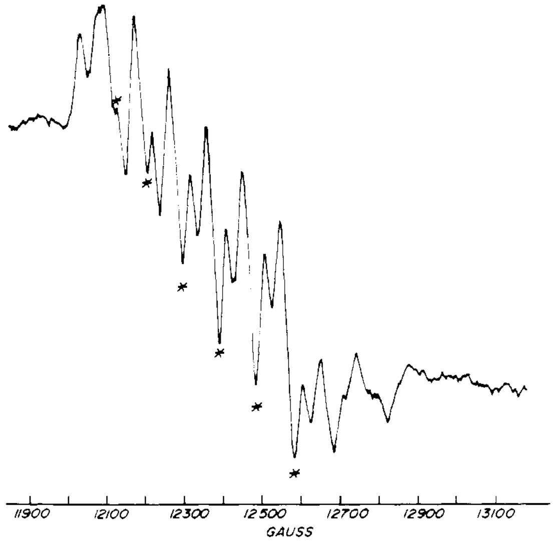

Figure 4. Q-Band electron spin resonance spectrum of PcMn(O_2) dissolved in *N,N*-dimethylacetamide at approximately 4 K. The starred peaks correspond to the "acid impurity" (see Figure 5). Of the many Q-band spectra recorded, this example showed the largest ratio of PcMn(O_2) to "acid-impurity" signal but also the poorest base line. Instrumental parameters: gain 3.2×10^3, frequency 34.616 GHz, pen response 3.0 s, power 18 db, acquisition time 16 min, modulation amplitude 10 G, range ca. 11500–13500 G.

from preparation to preparation and was often relatively very weak. We are therefore convinced that the $g = 4$–6 absorption does not belong entirely, if at all, to the adduct. It must arise from the presence of low concentrations of impurities or possibly small amounts of alternate oxygenated species. For example, a weak signal near $g = 4$ has 11 lines and presumably arises from a binuclear manganese species. Because of these signals it is not possible to exclude the possibility that the adduct has weak absorption in this area. We were unable to find any absorption due to the adduct at higher fields. The X-band spectrum appears to show three overlapping 6-line patterns but no obvious 11-line patterns. Some of the signal may arise from forbidden transitions which are common in manganese ESR spectra.[36] The Q-band spectrum (Figure 4) is simpler, showing two overlapping sextets plus additional weaker lines. Before discussing these data further, it is necessary to digress to consider a manganese-impurity ESR signal. The species[3] PcMn^{III}(OAc), most conveniently prepared by adding acetic acid to a DMA solution of the μ-oxo species, yields the moderately intense ESR spectrum shown in Figure 5 in the X and Q bands. This signal appears in many manganese(III) phthalocyanine samples especially if some free acid is present. Since a high-spin d^4 manganese(III) species will be ESR quiet[36] and the spectrum is typical of a cubic manganese(II) species, we assume that the signal arises from free manganese(II) in solution. It probably arises through a small percentage of acid-catalyzed demetalation of the ring, as has previously been observed with manganese porphyrins.[37,38] The Q-band spectrum of PcMn(O_2) (Figure 4) arises from a mixture of two species since the relative intensities of the two major sextets vary from one sample to another. One of these sextets (marked with an asterisk in Figure 4) has the same, free-spin, g and A_{Mn} values as the "acid impurity" and may be assumed to arise therefrom. The other sextet is associated

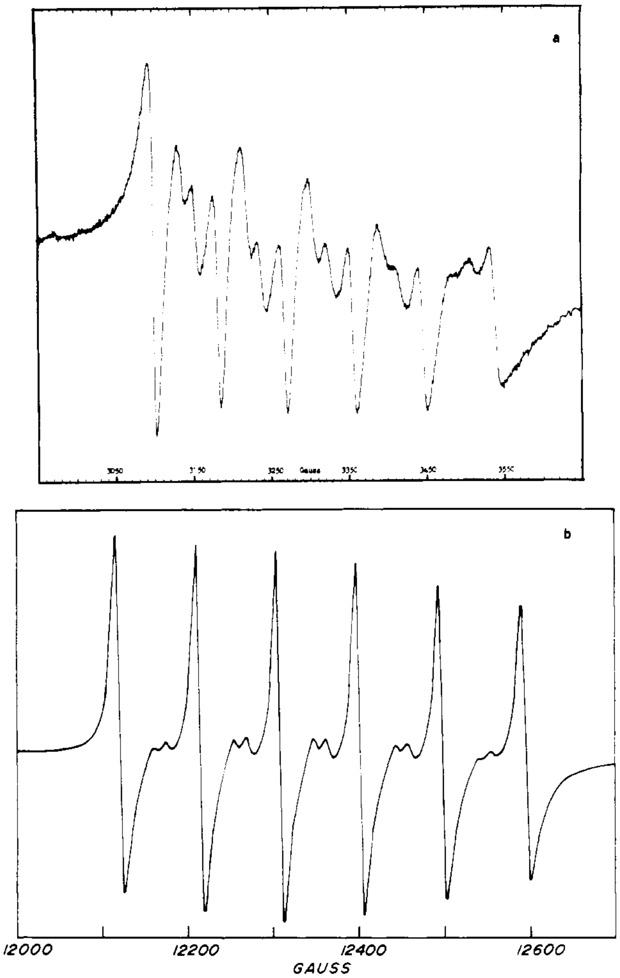

Figure 5. X- and Q-band spectra of the "acid impurity" obtained by addition of acetic acid to a solution of the μ-oxo species dissolved in *N,N*-dimethylacetamide at 4 K. The sextet is centered at $g = 2.004$ with $|A_{Mn}| = 0.0088$ cm^{-1}. (a) X-Band instrumental parameters: gain 1.25×10^4, frequency 9.1718 GHz, pen response 0.064 s, power 5 mW, acquisition time 4 min, modulation amplitude 8 G, range 3050–3600 G. (N.B.: The field was not accurately calibrated in this experiment. The g value derived therefrom is slightly below that calculated from the fully calibrated Q-band spectrum.) (b) Q-Band instrumental parameters: gain 8×10^2, frequency 34.661 GHz, pen response 0.1 s, power 18 db, acquisition time 8 min; modulation amplitude 5 G, range 12000–12700 G.

with the additional lines at higher field and arises from PcMn(O_2).

The complexity of the X-band spectrum of the oxygen adduct is such that a full computer fitting is necessary. It is appropriate, however, to propose a tentative first-order analysis of the spectrum. A sextet beginning at the first major line near 3020 G has $g = 2.01$ and $A = 0.0089$ cm^{-1} and, after allowance for second-order distortion, less evident in the Q-band spectrum, probably corresponds with the Q-band sextet. The last line in this sextet is near 3500 G. A second sextet begins at the second major line (near 3060 G) and has $g = 1.98$ and $|A| = 0.0089$ cm^{-1}. The outermost lines of the spectrum appear reasonably associated with a third **g** tensor with much larger hyperfine coupling, centered at $g = 1.98$ with $|A| = 0.014$ cm^{-1}. Evidently these last two **g** tensors are lost or obscured in the Q-band spectrum. Extra features in the X-band spectrum may be forbidden transitions.[39] The relative intensities of the spectrum are independent of preparation, and the "acid-impurity spectrum" seems obscured in the X band

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(39) Until a complete analysis is carried out, this interpretation seems more consistent with the previous suggestion[9] incorporating a seventh line.

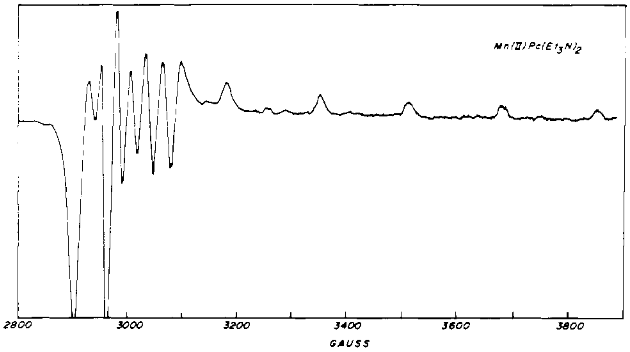

Figure 6. X-Band spectrum of manganese(II) phthalocyanine dissolved in *N,N*-dimethylacetamide in the presence of triethylamine at 80 K. The species in solution is low-spin ($S = {}^1/_2$) PcMn^{II}(Et$_3$N)$_2$. The signal characteristics are $g_\perp = 2.17$, $|A_\perp{}^{Mn}| = \sim 0.0036$ cm^{-1} and $g_\parallel = 1.89$, $|A_\parallel{}^{Mn}| = 0.015$ cm^{-1}. Instrumental parameters: gain 1.25 × 10^3, frequency 9.109 GHz, pen response 1 s, power 0.6 mW, acquisition time 4 min, modulation amplitude 0.8 G, range 2900–3500 G.

by the more intense adduct spectrum. However, such an analysis is not readily associated with an $S = {}^3/_2$ spin state unless we are simply observing transitions within the $M_s = \pm{}^1/_2$ state with all other transitions lost because of a large zero-field splitting. The adduct in the solid state shows only a broad unresolved signal at $g = 2$. The magnetic data show an unidentified interaction in the solid state, yielding temperature-dependent magnetic moments (see Experimental Section). However, other than changes in overall intensity, the ESR spectrum is independent of temperature from 4 K until above liquid-nitrogen temperature, when it becomes difficult to detect. It is entirely possible that the solution spectrum arises from a different spin state, presumably $S = {}^1/_2$, than is present in the solid complex. Low solubility precludes a solution magnetic measurement. Note that there is precedent for manganese giving rise to very complex spectra in X band and deceptively simple spectra in Q band.[40] A more detailed analysis must await planned $^{17}O_2$ studies. Finally, we point out that the PcMn(O$_2$) spectrum is quite different from low-spin d^5 manganese(II) phthalocyanines ($S = {}^1/_2$) as exemplified by the spectrum of PcMn^{II}(Et$_2$N)$_2$ in Figure 6. If the adduct spectrum does arise from $S = {}^1/_2$, it must be electronically quite different from tetragonal low-spin (Mn(II)) d^5 $S = {}^1/_2$. The μ-oxo species generates an ESR-quiet solution even at liquid-helium temperature.

Conclusions

Of the various electronic possibilities for a 1:1 adduct, viz., PcMn^{II}(O$_2$) (with $^1O_2$ or $^3O_2$), PcMn^{III}(O$_2^-$), and PcMn^{IV}(O$_2^{2-}$), only the superoxide species is fully consistent with the observed electronic, infrared, and magnetic data. It is true that the absorption spectra of manganese(IV) phthalocyanine species have not as yet been characterized, but it seems highly improbable they would be so similar to those of PcMn^{III}.

On the other hand, we note that the spectrum of (TPP)Mn(O$_2$), regarded to be a manganese(IV) peroxide derivative[4] from an ESR analysis, exhibits an electronic spectrum very similar to those of TPPMn^{III} derivatives.

In Figure 7 we show a tentative molecular orbital description based upon the electronic spectra of a series of oxygen adducts.[41] We assume a bent terminal end-on bound oxygen molecule and point group C_s. The bonding and antibonding π orbitals on the oxygen molecule are classified as horizontal (in the Mn–O$_2$ plane and the plane of the point group) and vertical, i.e., perpendicular to the Mn–O$_2$ plane, on the basis of an early description by Gray and co-workers.[42] The adduct binding energy is assumed to arise through interaction of the π^*_h orbital on an oxygen atom with an appropriate metal d orbital (2a′). The π^*_v orbital interacts with an orbital which has π symmetry with respect to the phthalocyanine plane. As is clear from Figure 7, a spin of ${}^3/_2$ arises naturally from the "superoxide" formulation on which this diagram is based. If level 4a″ is moved down the energy scale and placed below the d orbitals, it would contain two electrons and the preferred description, still with $S = {}^3/_2$, would apparently be Mn^{IV}/O$_2^{2-}$. However, it is evident that these are merely limits of approximation in viewing the molecule. The "superoxide" formulation requires that both levels 2a′ and 4a″ are located primarily on oxygen. If, in fact, the former is equally shared with manganese, then this would infer a population of only two electrons in the oxygen π^* orbitals and a description of the molecule as PcMn^{II}(O$_2$).[43] Note that the observed magnetism of dioxygen chromium, iron, and cobalt porphyrins, as cited above, is also derived readily from Figure 7 by addition of the appropriate number of electrons.

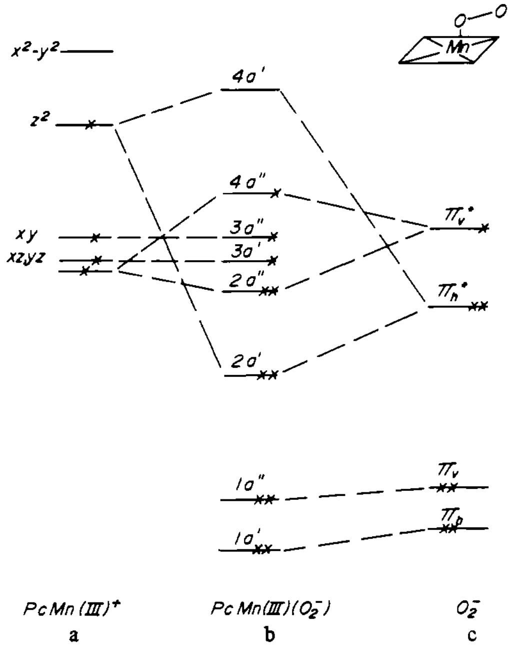

Figure 7. Qualitative molecular orbital diagram for PcMn^{III}(O$_2^-$): (a) d-orbital energy levels appropriate for a five-coordinate PcMn^{III}L unit; (b) MO levels for PcMn^{III}(O$_2^-$); (c) π and π^* levels of the superoxide ion. The relative order of the MO levels for the complex is based on both qualitative[42] and quantitative[44] molecular orbital treatments of dioxygen binding.

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Registry No. PcMn(O$_2$), 68027-09-8; HOMn^{III}Pc, 63105-50-0; PcMn^{II}, 14325-24-7; PcMn^{III}-O-Mn^{III}Pc, 12581-72-5; PcMn^{II}(*N*-Me-Im)$_2$, 76036-38-9; PcMn^{II}(Et$_3$N)$_2$, 76036-37-8.

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