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PHOTOCHEMISTRY OF MANGANESE COMPLEXES

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CONTENTS

A. INTRODUCTION

Photosynthesis provides the system whereby nature converts solar radiation into chemical free energy. The complexity of the photosynthetic unit of green plants is such that it is far beyond the realms of in vitro model systems. Hence in vitro studies are limited to relatively simple models of small parts of the whole. One part of the overall photosynthetic unit, namely the water oxidation process, is believed to involve an unidentified manganese complex [1]. Little is known about the role of manganese within the chloroplast; neither the environment, type of binding ligands, nor oxidation state of the metal ion are understood as yet. However, it seems feasible that the part played by manganese in the water oxidation process somehow involves redox changes of the metal. The formation of one molecule of oxygen from two molecules of water requires the transfer of four electrons. The only method available for transfer of all four electrons without involvement of intermediate free radicals is one based on charge accumulation. It is here that manganese is believed to be important.

Indeed, several speculative schemes have been proposed that describe the possible role of manganese. These schemes have been invoked to account for oxygen and proton yields obtained with sequential flashes of light [2]. Even so, there is no real evidence about the oxygen evolving site except that there seems to be about four manganese atoms per photosynthetic unit [3] and that the active manganese complex is probably EPR inactive [4]. Progress in this field is necessarily slow. However, a clear understanding of in vitro reactions of manganese complexes may help clarify the in vivo situation and help lead to a purely photochemical system for the capture and storage of solar energy. It is the aim of this review to describe the known photochemistry of manganese complexes. Particular emphasis has been given to photoredox processes, especially systems that may lead to oxidation of water.

B. OXYANIONS

(i) Stability

The higher oxidation states of manganese, Mn^V to Mn^{VII}, exist only in compounds containing oxide ligands. All Mn^{VII} compounds are strongly oxidising and only the permanganates are thermally stable at room temperature. The thermal stability of $KMnO_4$ has been extensively studied [5] but the products of reaction are still not completely assigned. The water soluble decomposition product is K_2MnO_4 but the water insoluble products remain uncertain [6,7]. Manganates(VI) are stable only in basic solution; acidification leads to disproportionation

$$3\ K_2MnO_4 + 2\ H_2O \rightarrow 2\ KMnO_4 + MnO_2 + 4\ KOH$$

Thermal decomposition produces [7] manganates(V) and other products. Manganates(V) [8] are even more prone to disproportionation than manganates(VI) and exist only in strongly basic solution.

$$3\ K_3MnO_4 + 2\ H_2O \rightarrow 2\ K_2MnO_4 + MnO_2 + 4\ KOH$$

K_3MnO_4 is much more stable thermally than either K_2MnO_4 or $KMnO_4$ and in dry air it appears to be stable up to about 900°C [7].

The oxyanions have been extensively studied by spectroscopists and theoreticians interested in the electronic absorption spectra and structure of these tetrahedral anions. All three anions show extensive absorption throughout the visible region; the absorption spectra are shown in Fig. 1. Oleari and co-workers [9,10] have conducted detailed MO calculations on all three anions. These calculations, together with earlier theoretical studies by Wolfsberg and

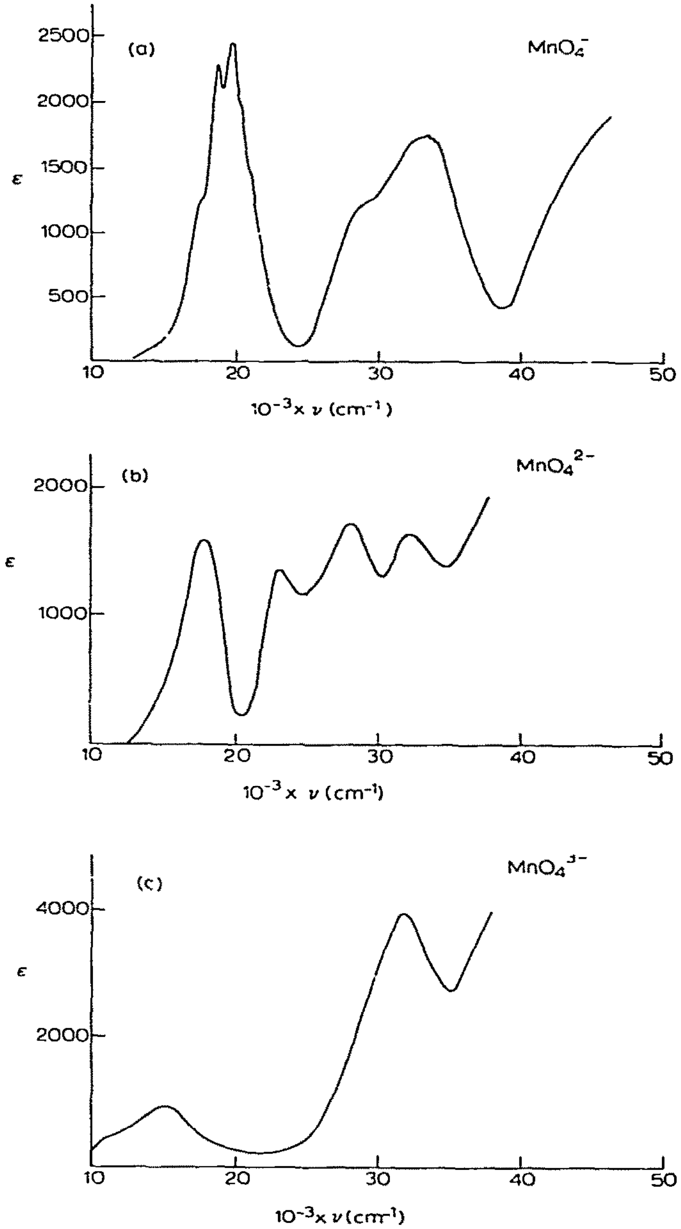


Fig. 1. Absorption spectra of the oxyanions in aqueous solution: (a) MnO_4^-; (b) MnO_4^{2-}; (c) MnO_4^{3-}.

Helmholtz [11] and Ballhausen and Liehr [12], provide an ordering of energy levels for the anions. The results of these calculations have been supported by EPR measurements by Carrington and co-workers [13—15].

(ii) Photochemistry

It has been known since the early work of Mathews and Dewey [16] in 1913, that neutral or alkaline solutions of permanganates are photochemically decomposed to give gaseous oxygen and either MnO_2 or MnO_4^{2-}, the final product depending upon pH. These qualitative studies were confirmed by later workers [17,18] but it was not until 1955 that Zimmerman [19] published quantitative data that enabled proposal of a reaction mechanism. Zimmerman [19] found that the quantum yield of O_2 formation was strongly dependent upon the excitation wavelength, slightly dependent upon temperature for excitation at long wavelengths only, and independent of pH, light intensity, and composition of the solution. The average Φ_{O_2} values obtained are given in Table 1 and vary between 0.05 for excitation at 254 nm and 10^{-5} for excitation at 578 nm. The temperature dependence was found only with excitation wavelengths above 436 nm, the strongest dependence being at the longest wavelength used (578 nm). An apparent activation energy of 4 kcal mol^{-1} was obtained from an Arrhenius plot [19]. Detailed isotopic studies showed conclusively that all the evolved O_2 came from permanganate ions without involvement of solvent molecules, so that the reaction is an intramolecular process. Zimmerman [19] considered the reaction to involve one of two processes

$$MnO_4^- \xrightarrow{h\nu} MnO_2 + O_2^- \tag{1}$$

or

$$MnO_4^- \xrightarrow{h\nu} MnO_2^- + O_2 \tag{2}$$

Later work by Klaning and Symons [20] using low temperature glasses showed that $KMnO_4$ was readily photolysed by 366 and 254 nm light to give tervalent manganese and O_2. Alcohol solvents were not attacked during the photolysis nor was there any evidence for involvement of free oxygen atoms. Using EPR techniques, it was shown [20] that O_2^- was not formed as a reaction intermediate so that process (2) is most probably correct. It should be

TABLE 1

Quantum yields for formation of oxygen upon photolysis of $KMnO_4$ in aqueous solution

λ(nm)	ϕ_{O_2}
254	0.055
313	0.0048
365	0.0023
405	0.0011
436	0.00016

noted that a process involving heterolysis of two bonds is uncommon in photochemical reactions.

The absorption spectrum of MnO_4^- (see Fig. 1) consists of three distinct bands. The short wavelength band shows no vibrational structure and may represent a CTTM transition. The other two bands show some vibrational structure, especially in the solid phase at low temperature. Zimmerman [19] used the absence of any observable luminescence as evidence for a very short excited state lifetime ($<10^{-12}$ s) so that either internal conversion or predissociation must occur with high probability. If excitation results in predissociation, the small quantum yields must be attributed to recombination of the two fragments within the solvent cage. The excitation wavelength and temperature dependence would then reflect the amount of excess energy available to the fragments to overcome geminate recombination. However, Zimmerman [19] preferred a mechanism in which internal conversion produces hot ground state MnO_4^- ions which dissociate thermally with a certain probability within the "cooling-off" period. Thus, the probability of dissociation (hence the quantum yield) should increase with decreasing wavelength since the ion has more energy available for bond breakage. When the excitation energy is close to the threshold energy required for dissociation, the amount of equilibrium thermal energy contained in the molecule before excitation to an excited state may be sufficient to influence the dissociation probability. Hence the observed temperature effect at long wavelength excitations [19].

Klaning and Symons [20] extended their work to include both manganate(VI) and manganate(V) ions. Both anions were found to be photochemically inert which seems surprising if the Zimmerman "hot ground state" mechanism [19] is correct. However, as these authors point out, the three anions have different shaped configurational coordinate curves for the ground and excited states. Also, there should be greater organisation of solvent molecules around the highly charged anions and the relative stabilities of the labile ions MnO_2^-, MnO_2^{2-}, and MnO_2^{3-} which must be formed upon elimination of O_2 may be important factors in governing the photoreactivity of the anions.

Adamson et al. [21] considered various alternative mechanisms to explain the observed photochemistry of permanganates. It was noted that the strongly wavelength dependent quantum yields could occur if the band irradiated is not itself photoreactive but contains some absorption from the tail of an adjacent band which is active. Also, it was suggested that an electron transfer process could be operative [21]

$$MnO_4^- \xrightarrow{h\nu} MnO_4 + e$$

However, no photoelectron formation was observed [22] following UV irradiation of MnO_4^{2-} so that it seems unlikely that MnO_4^- ions would emit electrons [23].

More recent work by Prout and Lownds [24] using solid samples of $KMnO_4$ shows that the photochemistry is similar in the highly ordered crystalline phase. However, no advance in understanding the overall reaction mechanism has been made in recent years.

C. MANGANESE(IV)

(i) Stability and luminescence

Mn^{IV} shows a more extensive ground state chemistry than the higher oxidation states but, in general, the compounds are not particularly stable. The great stability of MnO_2 is in fact due to its inherent insolubility; the other Mn^{IV} compounds are readily hydrolysed and reduced. There have been very few studies made of the photochemistry of Mn^{IV} compounds although the luminescence properties of Mn^{IV} have received a limited amount of study.

Mn^{IV} is isoelectronic with Cr^{III}; both have the $3d^3$ configuration, and as such would be expected to show similar absorption and emission spectra. Indeed, this has been found to be the case for Mn^{IV} when incorporated as an impurity in various host lattices. A particular difficulty with this work is that it is often very difficult to obtain Mn^{IV} complexes in a pure form. Since the lowest excited state is expected to be quite long lived, since it is a ^2E_g state, it is especially susceptible to impurity quenching. One set of complexes that can be isolated in a relatively pure form is the hexafluoride salts and these have been widely studied. The $^2E_g \rightarrow {}^4A_{2g}$ luminescence, which is spin-forbidden, can be readily detected in polycrystalline samples [25—29] at low temperature (Fig. 2). Emission from the potassium, rubidium, and cesium salts is quite long lived and decays with the same time constant (2.9 ms) [29]. The broad band in the emission spectrum shown in Fig. 2 cannot be assigned to a transition within the Mn^{IV} ion but its shape, position, and lifetime (0.4 ms) are comparable to the known properties of $KMnF_3$. Small traces of man-

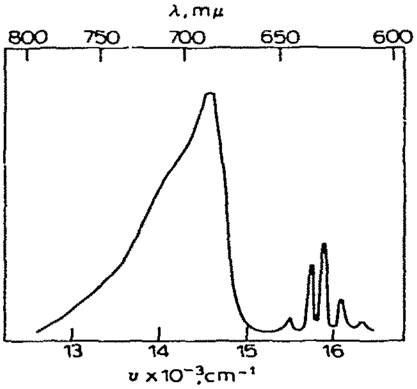


Fig. 2. Emission spectrum obtained from powdered K_2MnF_6 at low temperature; the broad part of the spectrum is believed due to a Mn^{II} impurity populated by energy transfer (from ref. 29).

ganese(II) are doubtless formed during the preparation of MnF_6^{2-} and it seems likely that the broad region of the spectrum is due to impurity emission arising from the $^4T_{1g} \rightarrow {}^6A_{1g}$ transition of MnF_3^- in the lattice. However, since the excited state levels of Mn^{II} could not be populated directly under the experimental conditions, an energy transfer process has been proposed [29].

(ii) Photochemistry

One of the few simple Mn^{IV} compounds is $Mn(SO_4)_2$ which is obtained by oxidising $MnSO_4$ in hot concentrated H_2SO_4 with permanganate. It is not particularly stable and is hydrolysed to MnO_2 even by dilute H_2SO_4. Dzhabiev et al. [30] have reported that $Mn(SO_4)_2$ oxidises water to molecular oxygen in acidic media. The reaction was studied in 6—15 M H_2SO_4 over a temperature range between 60 and 100°C. The amount of oxygen formed during the reaction was found to correspond to the equation

$$4\ Mn^{4+} + 2\ H_2O \rightarrow 4\ Mn^{3+} + O_2 + 4\ H^+$$

and the isotopic composition of oxygen liberated from ^{18}O enriched water was taken as evidence that oxygen came from water rather than sulphate ions [30]. Kinetic parameters were evaluated for reduction of Mn^{IV} and were interpreted in terms of reaction via dimeric $Mn^{IV} \cdot Mn^{IV}$, $Mn^{IV} \cdot Mn^{III}$, and $Mn^{III} \cdot Mn^{III}$ complexes. Three possible reaction mechanisms were considered by the authors [30]: (i) a one electron process with the intermediate formation of hydroxyl radicals from coordinated water molecules; (ii) a two electron process involving formation of hydrogen peroxide; (iii) a four electron reaction with direct formation of oxygen within the coordination sphere of a binuclear $Mn^{IV} \cdot Mn^{IV}$ complex. Although there was no experimental evidence cited, the authors [30] preferred the latter mechanism

$$Mn^{IV} \cdot Mn^{IV} + 2\ H_2O \rightarrow Mn^{II} \cdot Mn^{II} + O_2 + 4\ H^+$$

$$Mn^{II} \cdot Mn^{II} + Mn^{IV} \cdot Mn^{IV} \rightarrow 2\ Mn^{III} \cdot Mn^{III}$$

Later work by Dzhabiev and Shifirovich [31] showed that the above reaction could be enhanced by light. This is a particularly interesting result because of the importance of manganese in the natural photosynthetic oxygen evolution process, although the conditions used differ greatly to those found in nature. Under conditions where the dark reaction was negligibly slow, irradiation of $Mn(SO_4)_2$ in H_2SO_4 (6—10 M) with visible or near UV light (300—580 nm) at room temperature was reported [31] to result in generation of molecular oxygen and simultaneous reduction of Mn^{IV} to Mn^{III}. The kinetic patterns were found to be identical to the thermal reaction and, again, it was proposed that reaction involved a binuclear Mn^{IV} species [31] The quantum yield for the photoreduction of Mn^{IV} was found to be markedly dependent upon the excitation wavelength. The highest observed quantum yield was about 10^{-2} at 313 nm irradiation, falling to $<10^{-3}$ at 500 nm. On the basis of this wavelength dependence and a small temperature effect it was suggested [31] that the photochemical initiation of water oxidation could be attributed to reaction of hot ground state binuclear complexes, similar to the mechanism used by Zimmerman to account for the photochemistry of permanganate ions [19].

An important point to take into account with this work is that the nature of the $Mn(SO_4)_2$ species is uncertain. At best, it is a poorly characterised compound. Early work by Vetter and Manecke [32] and Lingane and Selim [33] has shown that $Mn(SO_4)_2$ will slowly oxidise water at room temperature unlike Ce^{4+} which is also thermodynamically capable of oxidising water [34]. Cerium(IV) does photooxidise water, forming oxygen and cerium(III) [35], although here the reaction involves intermediate free radicals. It has been proposed [36] that dimeric Ce^{4+} species were responsible for the observed reaction but Uri and Evans [37] were able to account for all the observed experimental data in terms of a simple mechanistic scheme

$$^{*}Ce^{4+} + H_2O \rightarrow Ce^{3+} + OH^{\cdot} + H^{+}$$

$$2\,OH^{\cdot} \rightarrow H_2O_2$$

$$2\,Ce^{4+} + H_2O_2 \rightarrow 2\,Ce^{3+} + 2\,H^{+} + O_2$$

This scheme also holds for the photooxidation of water by iron (III) [38] and seems to give a satisfactory account of the light enhanced oxidation of water by Mn^{IV}. Certainly, the experimental data described by Dzhabiev and co-workers [30,31] is not at variance with a mechanism involving formation of hydroxyl radicals for which the observed wavelength dependence can be attributed to the Franck—Rabinowitsch cage effect [39].

Mn^{IV} forms several binuclear complexes which have been fairly well characterised. The first reported complexes were the μ-dioxo-compounds formed with 2,2′-bipyridyl and 1,10-phenanthroline ligands as discovered by Turco and Nyholm [40]. Later workers reported similar μ-dioxo complexes with oxalate [41], Schiffs base [42], terpyridyl [43], gluconate [44], catecholate [45], and polyhydroxy [46] ligands. These complexes have been widely studied by polarography and undergo facile electrochemical reduction to the Mn^{III} and Mn^{II} complexes.

In 1974, Calvin [47] reported that UV photolysis of an aqueous solution of the mixed valence tetrakis(2,2′-bipyridyl)-μ-dioxo-dimanganese(III, IV) complex (Fig. 3) resulted in oxidation of water to molecular oxygen. However, this result was soon shown to be in error [48]. Later, Otsuji et al. [49] carried out a detailed study of the photochemistry of the compound in dilute H_2SO_4. These workers [49] found that an acidic solution of the $Mn^{IV}\cdot Mn^{IV}$ complex was gradually reduced to the $Mn^{IV}\cdot Mn^{III}$ complex upon standing in the dark. This mixed valence complex was stable in the dark but was rapidly reduced when irradiated with light $\lambda > 300$ nm. At this excitation wavelength, it is believed that irradiation populates a CTTM excited state; it is generally accepted that such excited states are responsible for many photoreduction processes. Under these conditions, the complex is rapidly photoreduced [49] to

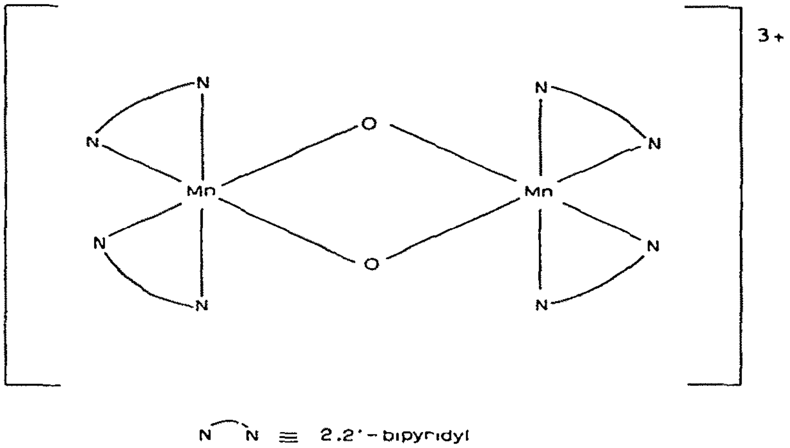
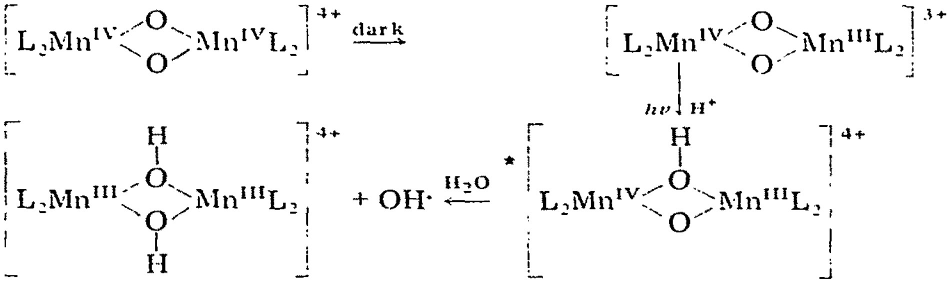
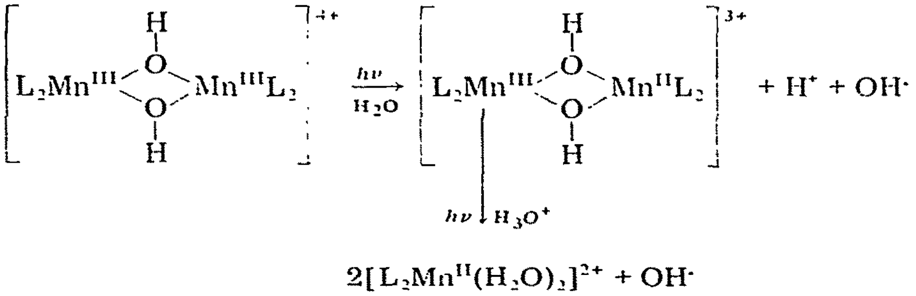


Fig. 3. Structure of tetrakis(2,2'-bipyridyl)-μ-dioxo-dimanganese(III, IV).

the $Mn^{III} \cdot Mn^{III}$ complex as monitored by absorption spectroscopy. The rate of reduction was found to increase with higher acid concentrations and a linear correlation between the reciprocal of the quantum yield for reduction and $1/[H^+]$ was obtained. These results were interpreted in terms of reduction occurring via a protonated excited state.



The $Mn^{III} \cdot Mn^{III}$ complex was further reduced upon irradiation [49]. The final product obtained was the Mn^{II} complex, again with concomitant formation of hydroxyl radicals.



Thus, at all stages, the reduction of the μ-dioxo complexes is always accompanied by the one electron oxidation of water to generate hydroxyl radicals and there is no formation of oxygen. Most, if not all, of the hydroxyl radicals so formed would be expected to form adducts with the aromatic ligands as observed with iron(III) [50] and ruthenium(III) [51] complexes. This one electron reduction of the binuclear complexes strengthens support for the idea that oxidation of water by $Mn(SO_4)_2$ also involves production of hydroxyl radicals. In the absence of aromatic ligands, hydroxyl radicals will combine to give hydrogen peroxide which is readily oxidised to molecular oxygen.

D. MANGANESE(III)

(i) Stability

Mn^{III} has a far more extensive ground state chemistry than any of the oxidation states so far discussed. There are relatively few simple compounds (only the acetate salt can be conveniently prepared) but Mn^{III} forms many stable complexes. Mn^{III} is a strong oxidising agent and in solution it is unstable with respect to disproportionation

$$2\ Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$$

$$Mn^{4+} + H_2O \rightarrow MnO_2 + 4\ H^+$$

Complexation of Mn^{III} with anions usually results in a lowering of the redox potential for the Mn^{III}/Mn^{II} couple. It is also known that the redox potential is dependent upon pH. Almost all the known complexes are anionic, such as the cyano complex, or neutral such as the β-ketonate compounds. Complexes formed with oxygen donor ligands have been known for some considerable time but complexes with nitrogen donors are much less common. Perhaps the best known examples of Mn^{III} complexes are the porphyrins and phthalocyanines but these compounds are described in a later section of the review.

(ii) Photochemistry

One of the earliest reported [52] photochemical investigations of Mn^{III} compounds concerned the low spin hexacyanide complex. However, the dark hydrolysis reaction is quite fast [53] and it is difficult to conclude to what extent, if any, light enhances the reaction [54]. Other workers [55] reported that the rapid exchange reactions between $Mn(CN)_6^{3-}$ and CN^- were not affected by light but, again, the dark reactions occur too quickly to make the photochemical study meaningful. The extensive photochemistry of the pentacyanonitrosyl complex $[Mn(CN)_5NO]^{3-}$ has been comprehensively reviewed by Balzani and Carassiti [23] and will not be elaborated upon here.

The most readily prepared complex of Mn^{III} is potassium trisoxalatomanganate(III). Like the corresponding iron(III) complex, the original preparation recommended that the synthesis be carried out in the dark because of problems with light sensitivity [56]. Quantitative experiments were undertaken by Porter et al. [57] who studied the light induced reactions at 0°C. At this temperature, thermal degradation is at a minimum but becomes very rapid if the solution is allowed to reach room temperature. Irradiation of the complex in aqueous solution leads to reduction of the manganese atom and formation of carbon dioxide as, in fact, does the thermal reaction

$$[Mn(C_2O_4)_3]^{3-} \xrightarrow{h\nu} [Mn(C_2O_4)_2]^{2-} + C_2O_4^{\cdot-}$$

$$[Mn(C_2O_4)_3]^{3-} + C_2O_4^{\cdot-} \rightarrow 2\ CO_2 + [Mn(C_2O_4)_2]^{2-} + C_2O_4^{2-}$$

In this respect, the photoreaction is identical to that proposed for several other first row transition metal oxalato complexes.

The quantum yield for photoreduction was observed by Porter et al. [57] to be dependent upon the excitation wavelength. This dependence is shown in Fig. 4 and is seen to fall into two distinct regions. At high energy irradiation, the quantum yield is independent of excitation wavelength. Here, the primary act leading to net decomposition must be the dissociation of a radical ion ligand from the reduced metal complex ion. Since the reduced product has no effect on the quantum yield, secondary recombination cannot be responsible for a primary quantum yield being less than unity. Similarly, if a cage effect were important then the quantum yield would be wavelength dependent in this excitation region. Thus, the relatively low quantum yield must be attributed to a degradative process, such as internal conversion, which competes directly with the dissociative reaction [57]. Since luminescence cannot be observed, the rate of any such degradative process must be of the order of $10^{10}\ s^{-1}$.

The wavelength at which the quantum yield starts to decrease matches the

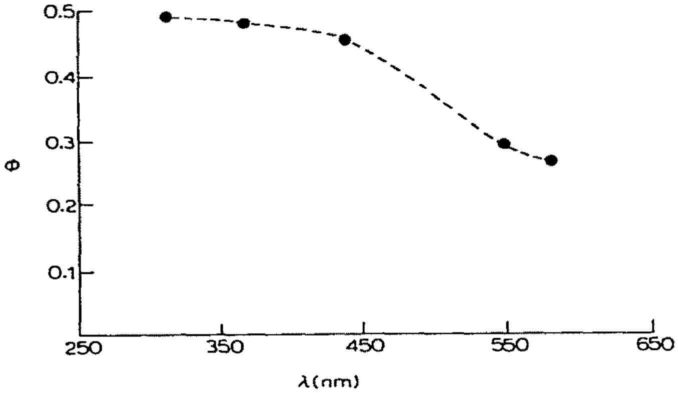


Fig. 4. Wavelength dependence for the quantum yield of photodecomposition of potassium tris(oxalato)manganate(III) in aqueous solution (from ref. 57).

minimum between the CT band and the first ligand field band. However, the quantum yield does not exactly follow the decreasing intensity of the CT band and absorption into the first ligand field band still leads to the photoredox reaction. At wavelengths above 500 nm, the CT band seems to contribute less than a few per cent towards the observed extinction coefficient but the quantum yield has fallen by only 25%. In solution, it is well known that extremely rapid internal conversion processes occur which degrade excited states to the lowest excited state of the same multiplicity. If this internal conversion process dominates the excited state behaviour then any subsequent reactions would have quantum yields independent of the excitation wavelength and the type of excited state populated by absorption. Since this is not the case observed here, the dissociation reaction must compete with or precede internal conversion. Furthermore, since the primary photoreaction involves a redox process it seems probable that the CT state is the reactive excited state even when absorption corresponds to a ligand field band. Porter et al. [57] considered that absorption from the CT band continued throughout the visible region although it was realised that the extinction coefficient would be necessarily low. To account for the observed wavelength dependence it was proposed that there was considerable mixing between the ligand field state and the CT state which allowed rapid non-radiative conversion from the former to the latter [57]. The decrease in quantum yield could then arise from either or both competition between interconversion of the two states and collisional internal conversion or a cage effect involving recombination of the primary fragments. This latter effect is believed to be important in the photochemistry of the iron(III) complex [58].

In a rigid glass at 77 K $[Mn(C_2O_4)_3]^{3-}$ is also decomposed by UV light. Although the characteristic absorption spectrum shows that efficient, irreversible destruction of the complex occurs it has been reported [59] that an EPR signal due to Mn^{2+} is only observed when the sample is warmed to 165 K. There was no further change in the absorption spectrum during this increase in temperature and a second EPR signal can be observed. This has been assigned to the oxalate radical ion. To explain this temperature effect, it has been proposed [59] that at 77 K the Mn^{2+} ion and the oxalate radical ion formed by the primary photoact are still bonded and are EPR inactive. Increasing the temperature to 165 K causes dissociation, hence resulting in the appearance of the two EPR signals. On further warming (above 170 K) the Mn^{2+} signal increased but the signal due to the oxalate radical ion disappeared, presumably due to thermal reaction with an unreacted molecule of $[Mn(C_2O_4)_3]^{3-}$ [59].

$$\begin{tikzcd}[Mn(C_2O_4)_3]^{3-} \arrow[r] & {[Mn^{II}(C_2O_4)_2(\ldots C_2O_4^-)]^{3-}} \arrow[d, "\Delta"] \\ & {[Mn(C_2O_4)_2]^{2-} + C_2O_4^{\overset{\cdot}{-}}}\end{tikzcd}$$

Several other Mn^{III} carboxylates are known to be photoreduced in solution. Thus, $[Mn(C_2O_4)_2(H_2O)_2]^-$, which is also thermally unstable, is reduced efficiently by light [60,61]

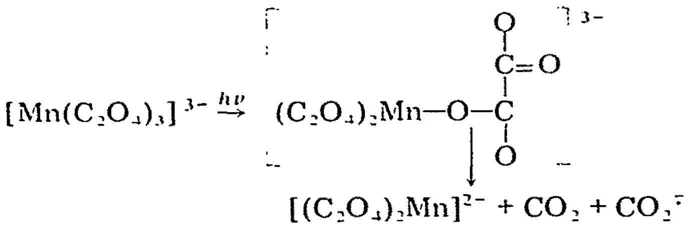
$$[Mn(C_2O_4)_2(H_2O)_2]^- \xrightarrow{h\nu} Mn^{2+} + CO_2 + 2\,H_2O + \tfrac{3}{2}C_2O_4^{2-}$$

The quantum yield for formation of CO_2 was measured to be 0.30. Similarly, Mn^{III} tartrate [62,63] and malonate complexes [64] undergo efficient photoredox reactions forming Mn^{2+} ions and an oxidised carboxylate derivative.

Similar photoredox reactions proceed in the solid phase but here the thermal stability of potassium trisoxalatomanganate(III) is greatly enhanced, in fact, the thermal stability is such that Simmons and Wendlandt [65] have proposed the use of this complex as an actinometer for solid state photochemistry. Upon UV irradiation, crystals of $K_3Mn(C_2O_4)_3$ change from deep red to white and the reaction can be easily monitored by reflectance spectroscopy. The stoichiometry of the products show that the photoreaction can be described [66]

$$2\,K_3[Mn(C_2O_4)_3]\cdot 3\,H_2O \xrightarrow{h\nu} 2\,K_2[Mn(C_2O_4)_2] + 2\,CO_2 + K_2C_2O_4 + 6\,H_2O$$

as has been found for the cobalt complex [67]. For irradiation at 400 nm, the quantum yield for loss of the Mn^{III} complex was found [68] to be 0.52 ± 0.09. This value was independent of light intensitv and, interestingly, it was about the same as that found for the corresponding aqueous solution at the same excitation wavelength [57]. Various mechanisms have been proposed for the solid state photoreactions which involve oxalate radical ions and bridged intermediates. Using EPR data, Simmons and Wendlandt proposed an overall mechanism involving a carbon dioxide radical ion [65]



$$[Mn(C_2O_4)_3]^{3-} \xrightarrow{h\nu} \left[(C_2O_4)_2Mn{-}O{-}\underset{\underset{O}{|}}{\overset{\overset{\overset{O}{|}}{C=O}}{|}}{C}\right]^{3-} \longrightarrow [(C_2O_4)_2Mn]^{2-} + CO_2 + CO_2^{\cdot-}$$

$$[Mn(C_2O_4)_3]^{3-} + CO_2^{\cdot-} \rightarrow [Mn(C_2O_4)_2]^{2-} + CO_2 + C_2O_4^{2-}$$

The solid state photoredox reactions of the complexes $K[Mn(mal)_2(H_2O)_2]$ [69], $K[Mn(mal)_2]$ [69], and $K_3[Mn(mal)_3]$ [70] have been investigated by Wendlandt and co-workers. In all cases, irradiation results in reduction to Mn^{II} and concomitant oxidation of one of the ligand molecules.

Poznyak et al. [71] have studied the photochemistry of a Mn^{III} complex in strong HCl solution. Normally, Mn^{III} complexes undergo disproportionation in solution but this was suppressed by addition of Mn^{II} ions. As is often the case, the actual structure of the Mn^{III} chloride complex was unknown; it was obtained by dissolving $CsMn(SO_4)_2$ in 11.5 M HCl.

The chloride complex showed absorption maxima at 555, 400 and 278 nm [71], the latter band being due to a CTTM transition. At 77 K, irradiation with UV light (λ ca. 350 nm) caused decomposition of the complex as monitored by absorption spectroscopy. At the same time, the $Cl_2^{\cdot -}$ radical could be observed by EPR and by its characteristic absorption bands at 340 and 680 nm. Thus, UV photolysis seems to result in intramolecular charge transfer [71].

$$Mn^{III}Cl_n \xrightarrow{h\nu} Mn^{II}Cl_{n-1} + Cl^{\cdot}$$

$$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot -}$$

A similar reaction has been reported with frozen solutions of iron(III) bromide [72].

Under identical reaction conditions but at room temperature, the chloride complex was apparently inert to photolysis with UV light [71]. However, the authors proposed that, in fact, the redox reaction does occur at room temperature but that the back reaction is very efficient. Evidence for the back reaction was obtained by separate experiments. Thus, a solution of the Mn^{III} complex was irradiated at 77 K and then warmed until the Cl_3^- band disappeared [71]. Upon warming, the original complex absorption spectrum returned together with a band at 232 nm due to Cl_3^-. Also, irradiation of a solution of HCl or Mn^{II} in strong HCl (both solutions were without Mn^{III}) with 254 nm light resulted in formation of $Cl_2^{\cdot -}$ (presumably by disproportionation) and in the presence of Mn^{II}, the characteristic absorption spectrum of the Mn^{III} chloride complex appeared. It was therefore concluded [71] that the photodecomposition of the Mn^{III} chloride complex was observed only because of a spatial separation that occurred at 77 K which stabilised the products.

E. MANGANESE(II)

(i) Stability

Mn^{II} is the most important and generally the most stable oxidation state of manganese. In neutral or acidic solution the pink hexaaquo ion is extremely resistant to oxidation but in strongly basic solution the hydroxide $Mn(OH)_2$ is formed and this compound can be readily oxidised by air. There are a wide variety of salts, most of which are soluble in water, and many complexes. The equilibrium constants for formation of the complexes are low because the Mn^{2+} ion is large and possesses no ligand field stabilisation energy. Although the normal coordination number of Mn^{II} is six, the halide complexes MnX_4^{2-} are tetrahedral. Also, Mn^{2+} ions are known to occupy tetrahedral sites in certain glasses and to substitute for Zn^{2+} in ZnO [73].

The majority of Mn^{II} compounds are high spin. In octahedral fields, the d^5 configuration gives spin-forbidden as well as parity-forbidden transitions; hence the very weak colour of the compounds. In tetrahedral fields, the transitions are still spin-forbidden but are no longer parity-forbidden. Thus, the tetrahedral compounds are somewhat more coloured, usually pale yellow/green.

(ii) Luminescence

Luminescence from high spin octahedral and tetrahedral Mn^{II} compounds in phosphors [74], silicates [75] and glasses [76] has been known for a long time. Octahedral complexes generally show phosphorescence which is attributed to the lowest energy transition $^4T_{1g} \rightarrow {}^6A_{1g}$. The tetrahedral complexes show a similar phosphorescence due to the $^4T_1 \rightarrow {}^6A_1$ transition. Usually, the emission occurs around 590—660 nm for octahedral complexes and around 500—540 nm for tetrahedral complexes. The emission band shows a pronounced Stokes shift due to the excited state having a smaller equilibrium internuclear distance than the ground state. This is due to the different number of antibonding electrons in the two configurations.

The most studied octahedral compounds are the fluorides. Holloway and Kestigian [77] found that the luminescence properties of MnF_2 crystals were dependent upon temperature. Changes occurred just below, and were apparently related with, the antiferromagnetic ordering at the Neel temperature. Later work [78] showed that the emission maximum, lifetime, and yield of crystalline MnF_2 and the alkali metal salts $MMnF_3$ varied as a function of temperature above 21 K. In the region of the Neel temperature (67 K) small changes were observed; the emission maximum moved from about 610 to 666 nm whilst the lifetime increased from 5 to 8 ms and the yield increased by about 40%. At approximately one half the Neel temperature larger and more strongly temperature dependent changes were observed; the emission maximum moved to 582 nm, the lifetime increased to 23 ms and the yield increased fivefold at 21 K. It was proposed [78] that the magnetic ordering affected the Stokes shift through the magnetoelastic effect thus causing the observed emission changes near the Neel temperature. A similar effect caused the low temperature emission changes when the excited Mn^{2+} ion became aligned with respect to the surrounding lattice. The strong temperature dependence observed in this region was then attributed to a coupling of the lattice distortion with the magnetic interaction of the excited Mn^{2+} ion [78]. This effect has been confirmed by recent work [79].

A further class of luminescent octahedral complexes to receive intensive study is the amine adducts of type $MnCl_2 \cdot$ amine $\cdot$ HCl. In the solid state, emission is centred around 650 nm whilst the lifetime is about 300 µs [80—82] (Table 2).

It has been known for some time that tetrahedral complexes of Mn^{II} show strong luminescence in the solid state [82]. In particular, the tetrahedral halide complexes MnX_4^{2-} exhibit intense spin-forbidden emission. Wrighton and Ginley [83] have reported on the luminescence from powdered MnX_4^{2-} ($X = Cl^-$, Br^- and I^-) complexes and have attributed the observed systematic changes in the decay rates to changes in the degree of spin orbital coupling

TABLE 2

Luminescence maxima and lifetimes for some octahedral Mn^{II} complexes of type $MnCl_2 \cdot$ amine $\cdot$ HCl

Amine	λ(nm)	τ(μs)
Aniline	670	370
p-Toluamine	658	170
Trimethylamine	655	270
Piperidine	653	320
Pyridine	650	30

induced by the halide ions. The crystalline samples show narrow, structureless emission centred around 510 nm which undergoes a slight sharpening upon cooling. The emission maximum and band shape appear to be independent of both X and the cation used. The luminescence quantum yields are high (Table 3) suggesting that a large fraction of the excited states follow radiative decay. The lifetimes show little dependence on temperature but are markedly different for the different halides. For X = Cl^-, the lifetime is the longest (about 2 ms); for X = Br^-, the lifetime falls to about 400 μs; and for X = I^- the lifetime is quite short (40 μs).

Both radiative and non-radiative rate constants followed the order $MnI_4^{2-} > MnBr_4^{2-} > MnCl_4^{2-}$ [83]. The observed enhancement in radiative decay rates for X = I^- relative to X = Cl^- can be attributed to either increased spin orbital coupling due to the heavier halide or to increased covalency in the Mn—X bond. However, the good overlap between absorption and emission spectra, the narrow emission band and the high emission yields suggest small changes in bonding upon electronic excitation [83]. Thus, although there are undoubted differences in the degree of covalency, the major factor responsible for the acceleration in rates of radiative decay is enhanced spin orbital coupling.

Several tetrahedral Mn^{II} complexes exhibit triboluminescence (i.e. the

TABLE 3

Luminescence maxima, quantum yields and lifetimes of tetrahedral MnX_4^{2-} complexes (as powdered solids)

Complex	λ 10^{-4} (cm^{-1})	τ (ms)	φ
$(Et_4N)_2MnCl_4$	1.91	2.0	0.32
$(Et_4N)_2MnBr_4$	1.91	0.35	0.53
$(Pr_4N)_2MnBr_4$	1.95	0.42	0.56
$(Me_4N)_2MnI_4$	1.88	0.047	0.27
$(Bu_4N)_2MnI_4$	1.86	0.040	0.29

emission of light caused by application of mechanical stress to crystals). This effect was first noted by Goodgame and Cotton [84]. Later work by Hardy and Zink [85] established the importance of the Mn^{II} complex used and assigned the observed luminescence to *dd* states of Mn. The usual emission spectrum of the complex and the triboluminescence spectrum were superimposable (Table 4). The absence of luminescence from $Mn(Ph_3PO)_2Cl_2$ is somewhat strange since triboluminescence could be detected readily. Hence, the technique of triboluminescence may be useful in determining excited state energy levels of non-luminescent transition metal compounds.

(iii) Photochemistry

Mn^{II} is very stable towards both thermal and photochemical reactions. As a consequence, there are few reports concerned with the photochemistry of Mn^{II} compounds. In fact, most reports simply attest to the photochemical stability of Mn^{II}. Thus UV irradiation of simple Mn^{II} salts in propan-2-ol [86], water [87], or HCl [71] gives no observable products arising from the metal ion. However, there are a few very early reports [88,89] that aqueous solutions containing Mn^{2+} ions and oxalate ions undergo photoreaction leading to the formation of CO_2. It has also been reported that Mn^{2+} ions can induce Eders reaction [90].

Recent work by Ferreira and Harriman [91] has shown that Mn^{II} undergoes inefficient photoionisation in dilute H_2SO_4. Flash spectroscopy showed the transient formation of Mn^{III} as evidenced by a broad absorption band at about 500 nm. Previously, Burroughs et al. [87] using the nitrate salt in water had not detected formation of Mn^{III}, hence the nature of the anion and the pH may be important properties in this reaction.

The low spin complex $Mn(CN)_6^{4-}$ is unaffected by light [54] but the nitrosyl complex $[Mn(CN)_5NO]^{3-}$ is photoactive. Irradiation in buffered solution leads to hydrolysis [92].

$$[Mn(CN)_5NO]^{3-} \xrightarrow[H_2O]{h\nu} Mn(H_2O)_6^{2+} + 5\ CN^- + NO$$

Quantum yields have not been reported but the reaction is markedly wave-

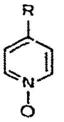
TABLE 4

Luminescence maxima, lifetimes and triboluminescence emission maxima for some tetrahedral Mn^{II} complexes

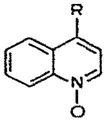
Complex	λ (nm)	τ (μs)	λ^{Tribo} (nm)
$Mn(Ph_3PO)_2Cl_2$	None	—	520
$Mn(Ph_3PO)_2Br_2$	500	602	500
$(MePh_3P)_2MnCl_4$	505	155	520
$(Et_4N)_2MnBr_4$	515	247	515
$(Bu_4N)_2MnI_4$	525	—	—

length dependent. It was found that irradiation at 254 nm was roughly three times as effective as at 366 nm whilst light of longer wavelength did not cause decomposition [92]. In the presence of added complexing anions such as CN^-, secondary thermal reactions lead to formation of complex ions such as $Mn(CN)_6^{4-}$.

Nathan et al. [93] have studied the photochemical reactions of Mn^{II} complexes formed with organic base N-oxides. The complexes used were $Mn^{II}L_6(ClO_4)_2$ where L =



or



and R = CH_3O, CH_3, H or Cl. The complexes are unstable to air and moisture [94] and are highly coloured. Irradiation of the powdered solids under N_2 or air leads to decomposition. Pyridine and quinoline were detected by GLC analysis whilst formation of Mn^{III} was observed by absorption spectroscopy, titration, and ion-exchange techniques [93]. Thus, irradiation results in intramolecular charge transfer.

Using cut-off filters, it was found that only irradiation into the CTTL band caused reaction, typical wavelengths being 380 nm for pyridine-N-oxides and 500 nm for quinoline-N-oxides. In contrast, photolysis of the gaseous N-oxides with light λ 254 nm forms pyridine or quinoline, a polymer and oxygen [95]. Quantum yields for decomposition of the Mn^{II} complexes were not measured but it required continuous irradiation for 122 h to achieve 10% decomposition, hence the quantum yields are probably very low. The substituent R had no observable effect except when R = NO_2 where there was no decomposition [93].

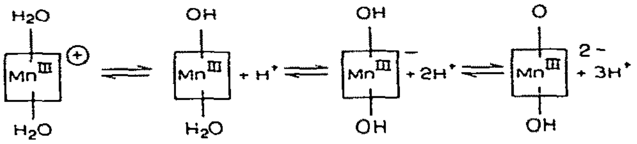
Photolysis in solution was complicated by the inherent thermal instability of the complexes. Thus, in acetonitrile the final product was MnO_2 formed by secondary thermal reaction between Mn^{III} and water present as a trace impurity [93].

F. PORPHYRIN AND PHTHALOCYANINE COMPLEXES

(i) Stability

The first manganese porphyrin was reported by Zaleski [96] in 1904. However, it was not until the work of Calvin and co-workers [97—100] some sixty years later that the nature of these complexes was established. The porphyrin ring is highly resistant to direct reaction and allows a central transition metal ion to participate in redox reactions. Thus, manganese porphyrins exist with formal Mn^{II}, Mn^{III} and Mn^{IV} oxidation states although the most stable complexes are those of Mn^{III}. The Mn^{II} complexes are readily prepared by reduction of the Mn^{III} complex with dithionite. However, these Mn^{II} complexes are oxidised rapidly by oxygen, reforming the original Mn^{III} complex. The Mn^{IV} complexes are the least stable and can only be observed in strongly basic solution. The best method for preparation of Mn^{IV} porphyrins is oxidation of Mn^{III} with persulphate or hypochlorite at pH 11.

All manganese porphyrins show intense absorption throughout the visible region. The most characteristic feature of the spectrum is the Soret band which, for a given porphyrin, varies markedly in position depending upon the oxidation state of the central manganese atom. For example with manganese tetrapyridylporphine the Soret band occurs at 441, 463 and 420 nm for Mn^{II}, Mn^{III} and Mn^{IV} respectively in aqueous solution. In addition to the tetradentate ligand, the manganese atom always has solvent molecules coordinated on to the axial positions. Thus, in the absence of excess electrolyte hydroxyl complexes are formed, the hydroxyl group being formed from residual water in the solvent. Since this hydroxyl group is acidic, there exists a series of acid/base forms.



Therefore, for any one particular manganese porphyrin there is a wide variety of possible structures in solution. The redox potentials of these different forms of the complex can vary so that the efficiency of a given redox reaction may be influenced greatly by the environment [97—100].

Manganese phthalocyanines were first investigated by Elvidge and Lever [101] and show significant oxygen binding properties. Again, the stable oxidation state is Mn^{III}. In general, the phthalocyanines behave identically to the porphyrins except for their very poor solubility in most solvents. However, water soluble derivatives are readily prepared by sulphonation.

The ground state chemistry of manganese porphyrin and phthalocyanine complexes has been reviewed in great depth by Boucher [102], Smith [103], and Lever [104].

(ii) Luminescence

There has been only one report concerning the luminescence of manganese porphyrins. Becker and Allison [105], during their investigation of the luminescence of metalloporphyrins, observed weak emission from a manganese porphyrin at low temperature. The porphyrin used was mesoporphine IX dimethyl ester and both Mn^{II} and Mn^{III} complexes were studied. The position of the emission bands was significantly different for the two complexes.

Emission from both complexes was short lived and very weak relative to the zinc derivative. In fact, Mn^{II} was somewhat more luminescent than Mn^{III}. The reason for poor yields and short lifetimes was believed to be due to rapid non-radiative decay which was enhanced by the paramagnetic metal centre.

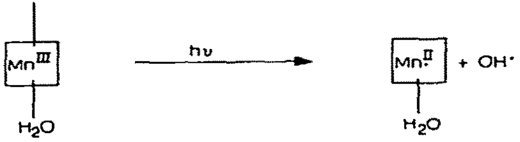
Becker and Allison [105] were concerned as to why the luminescence spectra from $\mathrm{Mn^{II}}$ and $\mathrm{Mn^{III}}$ complexes appeared to be so different spectrally. However, it must be realised that the structures of the two complexes are somewhat dissimilar. Thus $\mathrm{Mn^{II}}$ porphyrins are believed to be 5-coordinate [106]. That is, the $\mathrm{Mn^{II}}$ ion sits above the plane of the porphyrin ring and has only one coordinated solvent molecule. On the other hand, $\mathrm{Mn^{III}}$ seems to fit within the plane of the ring and has two axially liganded solvent molecules. In addition, the high-spin $\mathrm{Mn^{II}}$ complex, with its half-filled 3*d* shell, bears more resemblance to the diamagnetic zinc porphyrin than does $\mathrm{Mn^{III}}$. On this basis, it might be argued that the luminescence yield and lifetime of $\mathrm{Mn^{II}}$ porphyrins should be greater than the corresponding $\mathrm{Mn^{III}}$ porphyrins.

(iii) Photochemistry

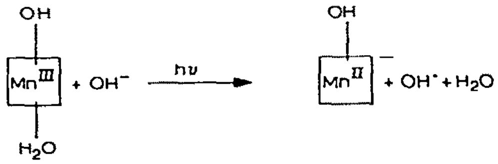
Manganese porphyrins are somewhat analogous to chlorophyll and as such have attracted the interest of several research groups. In general, it has been found that $\mathrm{Mn^{III}}$ porphyrins can be photoreduced to the corresponding $\mathrm{Mn^{II}}$ compounds with visible light. This reaction occurs with both porphyrins and phthalocyanines. The efficiency of photoreduction depends on the solvent and is highest in basic media. Under such conditions there is little or no dark reduction.

Engelsma et al. [97] have described in considerable detail the reactions of manganese phthalocyanine. It appears that $\mathrm{Mn^{III}}$ phthalocyanine is rapidly photoreduced in pyridine or dilute NaOH but that there is no apparent reduction in methanol, ethanol, or 1-chloronaphthalene. Later, Zavgorodnyaya and Glikman [107] reported that irradiation with visible light of an alkaline solution of $\mathrm{Mn^{III}}$ tetrasulphophthalocyanine resulted in formation of the $\mathrm{Mn^{II}}$ complex. Recently, Lever et al. [108] have confirmed that $\mathrm{Mn^{III}}$ phthalocyanine is smoothly reduced to $\mathrm{Mn^{II}}$ in vacuo by sunlight or by a photographic flash lamp. Quantum yields for the reduction reaction have been estimated for irradiation into the low energy absorption band [109] and were found to be about 0.05 in outgassed aqueous pyridine. Similar photoreductions have been reported for several $\mathrm{Mn^{III}}$ porphyrins, including pheophytin, pheophorbide and etioporphyrin complexes [107]. During all of the above experiments, there was no destruction of the chromophore, the only change being associated with the oxidation state of the central manganese atom.

It seems most probable that in aqueous solution hydroxide ions act as the electron donor so that the process results in formation of hydroxyl radicals. This reduction process may be intra- or intermolecular depending upon the concentration of base. Thus, at neutral pH, the electron donor is probably a coordinated ligand.



This reaction must be inefficient since it would be expected to occur in all solvents. At higher pH, uncomplexed hydroxide ions may serve as the electron donor.



This pH dependence has been studied in detail only for Mn^{III} chlorin [110]. Here, the quantum yield for photoreduction is very low, much lower than for the corresponding phthalocyanine, but increases from 1×10^{-5} at 0.01 M NaOH to 5×10^{-5} at 1 M NaOH. The quantum yield shows a small temperature and wavelength dependence which are consistent with a one electron redox reaction. After prolonged irradiation in 2 M NaOH, analysis showed the presence of hydrogen peroxide [110], the yield being about 60% of the stoichiometric amount.

$$2\,OH^{\cdot} \rightarrow H_2O_2$$

This is a surprisingly good balance since peroxide is known to react with manganese porphyrins [99].

It should be noted, however, that different acid/base forms of the complexes may be present at different pH values and these may have drastically different photoreduction efficiencies. Thus, the quantum yield versus pH profile may reflect changes in the intramolecular as well as the intermolecular reaction efficiency.

In a subsequent study, Glikman and Zavgorodnyaya [111] found that Mn^{II} porphyrins could be oxidised by quinones. Using Mn^{II} pheophorbide in basic solution, it was found that spontaneous oxidation to Mn^{III} occurred upon addition of either 1,4-benzoquinone or 1,4-naphthoquinone. However, 2-sulpho-9,10-anthraquinone (AQ) did not cause oxidation in the dark. When this latter system was irradiated with red light, semireduced quinone could be observed by absorption spectroscopy; a quantum yield of about 10^{-3} was estimated. It was proposed that under the experimental conditions any Mn^{III} pheophorbide produced would be rapidly photoreduced back to Mn^{II}

$$Mn^{II} + AQ \xrightarrow{h\nu} Mn^{III} + AQ^-$$

$$Mn^{III} + OH^- \xrightarrow{h\nu} Mn^{II} + OH^{\cdot}$$

Thus, it was claimed that this system provided a means of catalytically photooxidising water and photoreducing quinone [111].

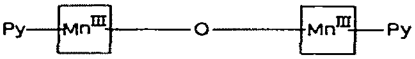
$$AQ + OH^- \xrightarrow{h\nu} AQ^- + OH^{\cdot}$$

Prolonged irradiation gave a concentration of semireduced quinone that was

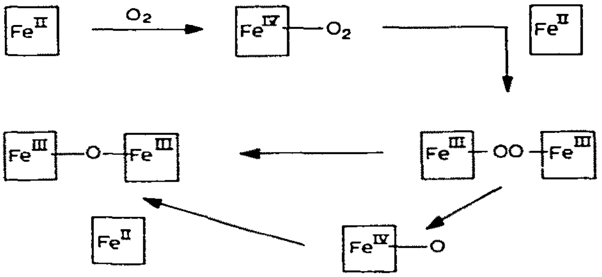
5.6 times the concentration of Mn^{II} pheophorbide originally present in solution. Furthermore, if Mn^{III} was used in place of Mn^{II} then after irradiation for some time, it was still possible to observe the appearance of semireduced quinone.

In a separate experiment it was noted that if an aqueous alkaline solution (0.4 M NaOH) containing an excess of AQ, Mn^{II} pheophorbide and chlorophyll in a proportion such that the latter absorbed >65% of the incident light, was irradiated with red light the rate of photooxidation of Mn^{II} increased relative to an experiment without chlorophyll. The quantum yield for formation of semireduced quinone increased about sixfold. This result was interpreted in terms of energy transfer from chlorophyll to the Mn^{II} pheophorbide. However, this explanation seems most unlikely and it is important to take into account direct reaction between photoexcited chlorophyll and AQ.

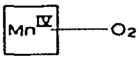
The ability of manganese phthalocyanine to reversibly bind oxygen has become well known since its discovery by Elvidge and Lever [101]. The usual method of oxygenating manganese phthalocyanine is to pass a steady stream of air through a solution in pyridine or alkaline ethanol. Prolonged aeration results in formation of μ-oxo-dimanganese(III) diphthalocyanine



which has been isolated in the crystalline form [112]. The structure of the oxygen adduct appears to be PcMn^{III}(O_2^{-}) [108], a precursor to formation of the μ-oxo dimer. In this respect there may be a resemblance with the autooxidation of iron porphyrins where magnetic spectroscopy has been used to identify some of the intermediate species [113]. The iron porphyrin system, although still speculative since neither of the iron(IV) species have been observed, has been described by the following scheme [113]



Manganese(II) porphyrins also reversibly bind oxygen in toluene solution at low temperature [114]. Here, EPR spectroscopy [115] and theoretical calculations [116] suggest that the oxygen adduct is a manganese(IV) peroxo species



which is analogous to the proposed iron(IV) adduct. However, there are several differences between the oxygen binding properties of manganese phthalocyanines and porphyrins, especially the importance of the solvent, and this field seems certain to attract much further work.

There is very little reported photochemistry of the oxygenated manganese phthalocyanine system and none at all for the porphyrin system. Thus, Lever et al. have found that the oxygen adduct is reconverted by sunlight in vacuo to oxygen and Mn^{II} phthalocyanine [108]. Also, Engelsma et al. [97] have shown that the μ-oxo dimer is reduced to Mn^{II} phthalocyanine upon irradiation in pyridine solution.

G. QUENCHING STUDIES

Simple transition metal ions have been found to quench electronically excited states in fluid solution. Several mechanisms may contribute to the overall quenching process, the important quenching mechanisms being paramagnetic quenching, electron transfer and energy transfer. All three processes have been shown to operate when the quencher is a Mn^{2+} ion.

Porter and Wright [117] were the first to present a detailed report describing the quenching of an excited state by Mn^{2+} ions. These authors studied the effects of several first row transition metal ions on the triplet lifetime of naphthalene in water and ethylene glycol solution. With all transition metal ions studied, the quenching rate constants were low, typically being about $<10^7$ M^{-1} s^{-1}. The results were explained in terms of the paramagnetic ion enhancing nonradiative decay processes of the triplet state [117]. This is really catalysed spin conversion and is quite independent of magnetic susceptibility provided the quencher is not a singlet. The quenching process can be considered to occur in two steps: (i) formation of a collision complex and (ii) subsequent dissociation of this complex to ground state reactants. The overall quenching rate constant should then depend upon spin—spin coupling between the two components, the lifetime of the collision complex, and a spin statistical factor. Porter and Wright calculated that the spin statistical factor was 1/3 for all systems whereby a triplet excited state was quenched by a transition metal ion. Thus, differences in the observed quenching rate constant between different quencher molecules were explained in terms of spin—spin interaction and the lifetime of the collision complex. These two factors are closely related since they both depend on the overlap of the orbitals of the unpaired electrons in the quencher and quenchee. With all transition metal ions this interaction is small, hence the low quenching rate constants.

Linschitz and Pekkarinen [118] extended the paramagnetic quenching theory to include some degree of charge transfer interaction. In a study of the quenching of triplet states of anthracene and porphyrins by heavy metal ions it was observed that Mn^{2+} was a particularly poor quencher compared to other transition metal ions. It was concluded that quenching resulted in formation of a CT intermediate although the extent of charge separation may be quite small. In this manner, it was possible to explain the observed solvent dependence. In the particular case of Mn^{2+}, the relatively low quenching rate constant was believed to be associated with the special stability of the half-filled 3*d* shell. A similar process was invoked to explain the effects of transition metal ions on the singlet state. Here, quenching probably leads to enhanced intersystem-crossing to the triplet manifold.

Brown et al. [119] reported the effects of Mn^{2+} complexes on the excited singlet and triplet states of chlorophyll in aqueous ethanol solution. The Mn^{2+} complexes quenched both singlet and triplet states although singlet quenching was some hundredfold more efficient than triplet quenching. The observed quenching rate constants are collected in Table 5 and show a marked dependence on the structure of the complex. In fact, an excellent linear correlation was found between log quenching rate constant and the redox potential of the quencher. Under these conditions, energy transfer can be neglected and there were no transient redox products detected by flash spectroscopy. Therefore, net electron transfer does not occur even for the most efficient case and quenching was attributed to paramagnetic enhancement of non-radiative decay of the excited state.

Similar quenching effects have been noted by other authors. Ledger and Porter [120] have reported that Mn^{2+} ions quenched triplet benzophenone in aqueous solution with a bimolecular rate constant of 8.3×10^7 M^{-1} s^{-1}. Ferreira and Harriman [91] found that Mn^{2+} was an inefficient quencher of triplet thionine (T) in weakly acidic solution. The observed triplet quenching rate constant (7×10^5 M^{-1} s^{-1}) was in the same range as that observed with other chromophores (see Table 6). Again, net electron transfer did not take place. However, different results were obtained when the Mn^{2+} ion was excited directly. Here semireduced thionine (T^-) and Mn^{3+} were observed by flash spectroscopy.

$$^*Mn^{2+} + T \rightarrow Mn^{3+} + T^-$$

The kinetics were complex since in addition to rapid back electron transfer

$$Mn^{3+} + T^- \rightarrow Mn^{2+} + T$$

there was a small amount of direct photoionisation of Mn^{2+} [91].

$$^*Mn^{2+} \rightarrow Mn^{3+} + e$$

Burroughs et al. [87] have investigated the effects of a wide range of metal ions on the luminescent state of the uranyl ion (UO_2^{2+}) in aqueous solution. The quenching process was shown to be dynamic and the correlation between log quenching rate constant and the ionisation potential of the metal was taken as evidence for electron transfer being the predominant mechanism. With Mn^{2+} as quencher, flash spectroscopy showed formation of a broad transient having an absorption maximum at about 505 nm. This transient was

TABLE 5

Rate constants for quenching singlet and triplet excited states of chlorophyll in aqueous ethanol solution

Quencher	k_S $10^{-8}(M^{-1}s^{-1})$	k_T $10^{-6}(M^{-1}s^{-1})$	$-E_{1/2}$ (V)
$Mn(H_2O)_6^{2+}$	1.5	1.6	1.51
$Mn(en)_3^{2+}$	4.0	4.2	1.44
$Mn(acac)_2^{2+}$	3.7	6.5	1.40
$Mn(bipy)_3^{2+}$	7.2	16.0	1.32
$Mn(phen)_3^{2+}$	9.2	60.0	1.25

identified as Mn^{3+} so that quenching appears to result in net electron transfer [87]

$$^*UO_2^{2+} + Mn^{2+} \rightarrow UO_2^+ + Mn^{3+}$$

This reaction seems to be the first reported sensitised photooxidation of a simple Mn^{2+} compound to the corresponding Mn^{3+} species.

Recent work by Duncan et al. [121] has been concerned with the thionine sensitised photochemistry of manganese gluconate complexes. Here, manganese(II) forms only a weak complex with the gluconate ligand and the complex is not oxidised by triplet thionine. However, the manganese(III) complex is more reactive. Previous work by Sawyer and co-workers [44,122] suggests that manganese(III) gluconate adopts a binuclear structure in solution (Fig. 5). Using flash photolysis techniques, Duncan et al. [121] were able to show that triplet thionine oxidised the ground state $Mn^{III} \cdot Mn^{III}$ complex to the mixed valence $Mn^{IV} \cdot Mn^{III}$ complex. It was not possible to observe formation of the fully oxidised $Mn^{IV} \cdot Mn^{IV}$ complex, even at high pH where the oxidised pro-

TABLE 6

Compilation of rate constants for quenching triplet excited states by $Mn(H_2O)_6^{2+}$ ions in fluid solutions

Triplet	Solvent	k_T $(M^{-1}s^{-1})$	Ref.
Naphthalene	H_2O/glycol	2.8×10^7	117
Anthracene	pyridine	4.3×10^6	118
Tetraphenylporphine	pyridine	$<5 \times 10^5$	118
Phenanthrene	H_2O/CH_3OH	$<4 \times 10^4$	123
Benzophenone	H_2O	8.3×10^7	120
UO_2^{2+}	H_2O	3.4×10^6	87
Chlorophyll	H_2O/C_2H_5OH	1.6×10^6	119
Thionine	H_2O	7×10^5	91

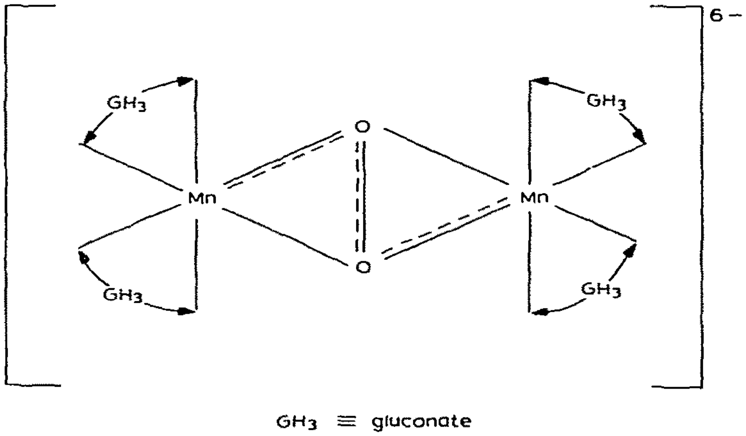


Fig. 5. Proposed structure for manganese(III) gluconate in alkaline aqueous solution.

duct is more stable with respect to water. Steady-state irradiation studies using an oxygen sensitive electrode showed the absence of oxygen formation with this system.

The Mn^{2+} ion is a particularly useful quencher for these experiments since it does not possess low energy excited states. With most transition metal ions it is always necessary to consider that quenching may occur by an energy transfer mechanism. This need not be so with Mn^{2+}. Thus, Marshall et al. [123] have reported the ineffective quenching of triplet phenanthrene by Mn^{2+} at temperatures ranging between 120 and 293 K. Under identical conditions, Co^{2+}, Ni^{2+} and Cu^{2+} acted as reasonably efficient quenchers; in each case the mechanism was believed to proceed by energy transfer. Similarly, Ballardini et al. found that $MnCl_2$ did not quench either the phosphorescence [124] or the photoaquation [125] of tris(ethylenediamino)chromium(III) under conditions where both $CoCl_2$ and $FeCl_2$ were effective quenchers. The phosphorescence of $Cr(en)_3^{3+}$ arises from the ^2E_g state whilst the photoaquation appears to occur from the higher energy quartet state which is in thermal equilibrium with the doublet. Consideration of the redox potentials of the three metal ions shows that the ineffective quenching by Mn^{2+} is inconsistent with a charge transfer quenching mechanism since Mn^{2+} and Co^{2+} have similar E^0 values. By the same type of argument, paramagnetic enhanced nonradiative decay cannot be a significant contributor to the quenching mechanism. However, both Fe^{2+} and Co^{2+} have low-lying excited states, at about 8.3 kK and 8.0 kK respectively in water, and can accept electronic energy from the doublet state of $Cr(en)_3^{3+}$ which is situated at about 15 kK. On the other hand, Mn^{2+} has its lowest energy level at about 19.5 kK so that energy transfer in this system is most improbable.

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REFERENCES

1 G.M. Cheniae, Annu. Rev. Plant Physiol., 21 (1970) 467.
2 G. Renger, Eur. J. Biochem., 27 (1972) 259.
3 G.M. Cheniae and I.F. Martin, Biochim. Biophys. Acta, 197 (1970) 219.
4 R.E. Blankenship and K. Sauer, Biochim. Biophys. Acta, 357 (1974) 252.
5 W. Levason and C.A. McAuliffe, Coordin. Chem. Rev., 7 (1972) 353.
6 H. Peters, K.H. Radeke and L. Till, Z. Anorg. Allg. Chem., 1 (1966) 346.
7 F.H. Herbstein, G. Ron and A. Weissman, J. Chem. Soc. A, (1971) 1821.
8 H. Lux, Z. Naturforsch., 1 (1946) 281.
9 L. Oleari, G. De Michelis and L. Di Spiro, Mol. Phys., 10 (1965) 111.
10 L. Oleari, G. De Michelis, L. Di Spiro and E. Tondello, Coordin. Chem. Rev., 2 (1967) 53.
11 M. Wolfsberg and L. Helmholtz, J. Chem. Phys., 20 (1952) 837.
12 C.J. Ballhausen and A.D. Liehr, J. Mol. Spectrosc., 2 (1958) 342.
13 A. Carrington and M.C.R. Symons, J. Chem. Soc., (1960) 88.
14 A. Carrington and D.B. Schonland, Mol. Phys., 3 (1960) 331.
15 A. Carrington and C.K. Jorgensen, Mol. Phys., 4 (1961) 395.
16 J.H. Mathews and L.H. Dewey, J. Phys. Chem., 17 (1913) 211.
17 E.K. Rideal and R.G.W. Norrish, Proc. Roy. Soc., Ser. A, 103 (1923) 342.
18 A.L. Sundara, Proc. Indian Acad. Sci., Sect. A, 6 (1937) 293.
19 G. Zimmerman, J. Chem. Phys., 23 (1955) 825.
20 U. Klaning and M.C.R. Symons, J. Chem. Soc., (1959) 3269.
21 A.W. Adamson, W.I. Waltz, E. Zinato, D.W. Watts, P.D. Fleischauer and R.D. Lindholm, Chem. Rev., 68 (1968) 541.
22 S. Ohno, Bull. Chem. Soc. Jpn., 40 (1967) 1779.
23 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York, 1970, p. 143.
24 E.G. Prout and C.M. Lownds, Inorg. Nucl. Chem. Lett., 9 (1973) 377.
25 S.A. Pollack and R.A. Satten, J. Chem. Phys., 36 (1962) 804.
26 R.A. Satten, J. Chem. Phys., 40 (1964) 1200.
27 C.D. Flint, J. Mol. Spectrosc., 37 (1971) 414.
28 L. Chodos, A.M. Black and C.D. Flint, Chem. Phys. Lett., 33 (1975) 344.
29 A. Pfeil, Spectrochim. Acta, Part A, 26 (1970) 1341.
30 T.S. Dzhabiev, V. Ya. Shifirovich and A.E. Shilov, React. Kinet. Cat. Lett., 4 (1976) 11.
31 T.S. Dzhabiev and V.Ya. Shifirovich, React. Kinet. Cat. Lett., 4 (1976) 419.
32 K.J. Vetter and G. Manecke, Z. Phys. Chem. (Leipzig), 195 (1950) 337.
33 J.J. Lingane and R.G. Selim, Anal. Chem. Acta, 21 (1959) 536.
34 L.J. Heidt and A.F. McMillan, J. Am. Chem. Soc., 76 (1954) 2135.
35 B.Y. Dain and A.A. Kachan, Dokl. Akad. Nauk SSSR, 67 (1949) 85.
36 L.J. Heidt and M.E. Smith, J. Am. Chem. Soc., 70 (1948) 2476.
37 N. Uri and M.G. Evans, Nature (London), 166 (1950) 602.
38 E. Collinson, F.S. Dainton and B. Holmes, Nature (London), 165 (1950) 267; M.G. Adamson, D.L. Baulch and F.S. Dainton, Trans. Faraday Soc., 58 (1962) 1388.
39 I. Franck and E. Rabinowitsch, Trans. Faraday Soc., 30 (1934) 120.

40 A. Turco and R.S. Nyholm, Chem. Ind., (1960) 74.
41 Y. Yoshino, I. Taninaga, M. Kokiso and T. Uchiro, Bull. Chem. Soc. Jpn., 47 (1974) 2787.
42 L.J. Boucher and C.G. Coe, Inorg. Chem., 14 (1975) 1289.
43 M.M. Morrison and D.T. Sawyer, Inorg. Chem., 17 (1978) 333.
44 M.E. Bodini and D.T. Sawyer, J. Am. Chem. Soc., 98 (1976) 8366.
45 K.D. Magers, C.G. Smith and D.T. Sawyer, J. Am. Chem. Soc., 100 (1978) 989.
46 K.D. Magers, C.G. Smith and D.T. Sawyer, Inorg. Chem., 17 (1978) 515.
47 M. Calvin, Science, 184 (1974) 375.
48 S.R. Cooper and M. Calvin, Science, 185 (1975) 376.
49 Y. Otsuji, K. Sawada, I. Morishita, Y. Taniguchi and K. Mizuno, Chem. Lett., (1977) 983.
50 J.W. Bunting and W.G. Meathrel, Can. J. Chem., 51 (1973) 1965.
51 C. Creutz and N. Sutin, Proc. Nat. Acad. Sci. U.S.A., 72 (1975) 2858.
52 R. Schwarz and K. Tede, Chem. Ber., 60B (1927) 69.
53 W.D. Treadwell and W.E. Raths, Helv. Chim. Acta, 35 (1952) 2275.
54 A.G. MacDiarmid and N.F. Hall, J. Am. Chem. Soc., 75 (1953) 5204.
55 A.W. Adamson, J.P. Welker and W.B. Wright, J. Am. Chem. Soc., 73 (1951) 4786.
56 C.H. Cartledge and W.P. Ericks, J. Am. Chem. Soc., 58 (1936) 2061.
57 G.B. Porter, J.G.W. Doering and S. Karanka, J. Am. Chem. Soc., 84 (1962) 4027.
58 C.A. Parker and C.G. Hatchard, J. Phys. Chem., 63 (1959) 22.
59 A.L. Poznyak, G.A. Shagisultanova and L.N. Neokladnova, Teor. Eksp. Khim., 4 (1968) 567.
60 I.G. Murgulescu, T. Oncescu and Z. Simon, Rev. Roum. Chim., 12 (1967) 737, 755.
61 B. Rackow, Z. Chem., 5 (1965) 397.
62 T.N. Srivastava, Z. Phys. Chem. (Leipzig), 233 (1966) 103, 110, 113.
63 N. Tanaka, Y. Kikuchi and Y. Usui, Z. Phys. Chem. (Frankfurt am Main) 37 (1963) 133.
64 J.I. Bullock, M.M. Patel and J.E. Salmon, J. Inorg. Nucl. Chem., 31 (1969) 415.
65 E.L. Simmons and W.W. Wendlandt, Coordin. Chem. Rev., 7 (1971) 11.
66 W.W. Wendlandt and E.L. Simmons, J. Inorg. Nucl. Chem., 28 (1966) 2420.
67 H.E. Spencer, J. Phys. Chem., 73 (1969) 2316.
68 E.L. Simmons and W.W. Wendlandt, Anal. Chim. Acta, 53 (1971) 81.
69 C. D'Ascenzo and W.W. Wendlandt, J. Inorg. Nucl. Chem., 32 (1970) 3109.
70 V.E. Stel'mashok, A.L. Poznyak and S.I. Arzhankov, Koord. Khim., 3 (1977) 524.
71 A.L. Poznyak, V.E. Stel'mashok and V.K. Rumas, High Energy Chem. (USSR), 11 (1977) 404.
72 V.F. Plyusnin and N.M. Bazhin, High Energy Chem. (USSR), 8 (1974) 316.
73 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry. Wiley Interscience, New York, 1972, p. 846.
74 P. Pringsheim, Fluorescence and Phosphorescence, Interscience, New York, 1948, Chapter VII.
75 H.W. Leverenz, Proc. Inst. Radio Eng., (1944) 256.
76 N.J. Kreidl, J. Opt. Soc. Am., 35 (1945) 249.
77 W.W. Holloway and M. Kestigian, Phys. Rev. Lett., 13 (1964) 235.
78 W.W. Holloway, E.W. Prohofsky and M. Kestigian, Phys. Rev., 139 (1965) 954.
79 J.M. Flaherty and B. Di Bartolo, in F. Williams (Ed.), Luminescence of Crystals, Molecules and Solutions, Plenum Press, New York, 1973, p. 388.
80 S.H. Linwood and W.A. Weyl, J. Opt. Soc. Am., 32 (1942) 443.
81 L.E. Orgel, J. Chem. Phys., 23 (1955) 1958.
82 G.B. Porter and H.L. Schlafer, Ber. Bunsenges. Phys. Chem., 68 (1964) 316.
83 M. Wrighton and D. Ginley, Chem. Phys., 4 (1974) 295.
84 D.M.L. Goodgame and F.A. Cotton, J. Chem. Soc., (1961) 3735.
85 G.E. Hardy and J.I. Zink, Inorg. Chem., 15 (1976) 3061.

86 E.F. Abdrashitov and L.A. Tikhomirov, High Energy Chem. (USSR), 10 (1976) 356.
87 H.D. Burroughs, S.J. Formosinho, M.G. Miguel and F.P. Coelho, J. Chem. Soc. Faraday I, 72 (1976) 163.
88 O.T. Christensen, Z. Anorg. Allg. Chem., 27 (1901) 321.
89 B.K. Mukerji and N.R. Dhar, Q.J. Indian Chem. Soc., 5 (1928) 203.
90 S. Sakuraba and S. Ikeya, Bull. Chem. Soc. Jpn., 30 (1957) 662.
91 M.I.C. Ferreira and A. Harriman, J. Chem. Soc. Faraday I, 73 (1977) 1085.
92 W. Jakob and T. Senkowski, Rocz. Chem., 40 (1966) 1601.
93 L.C. Nathan, J. Cullen and R.O. Ragsdale, Inorg. Nucl. Chem. Lett., 12 (1976) 137.
94 W.M. Reiff and W.A. Baker, Inorg. Chem., 9 (1970) 570.
95 N. Hata and I. Tanaka, J. Chem. Phys., 36 (1962) 2076.
96 J. Zaleski, Z. Physiol. Chem., 43 (1904) 11.
97 G. Engelsma, A. Yamamoto, E. Markham and M. Calvin, J. Phys. Chem., 66 (1962) 2517.
98 P.A. Loach and M. Calvin, Biochemistry, 2 (1963) 361.
99 P.A. Loach and M. Calvin, Biochim. Biophys. Acta, 79 (1964) 379.
100 A. Yamamoto, L.K. Phillips and M. Calvin, Inorg. Chem., 7 (1968) 847.
101 J.A. Elvidge and A.B.P. Lever, Proc. Chem. Soc., (1959) 195.
102 L.J. Boucher, Coordin. Chem. Rev., 7 (1972) 289.
103 K.M. Smith, Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975.
104 A.B.P. Lever, Advan. Inorg. Chem. Radiochem., (1965) 27.
105 R.S. Becker and J.B. Allison, J. Phys. Chem., 67 (1963) 2662.
106 B. Gonzalez, J. Kouba, S. Yee, C.A. Reed, J.F. Kirner and W.R. Scheidt, J. Am. Chem. Soc., 97 (1975) 3247.
107 L.N. Zavgorodnyaya and T.S. Glikman, Zh. Obshch. Khim., 39 (1969) 1443.
108 A.B.P. Lever, J.P. Wilshire and E. Quan, J. Am. Chem. Soc., 101 (1979) in press.
109 A. Harriman, unpublished results, 1977.
110 T.S. Glikman and O.V. Zabroda, Biokhimiya, 34 (1964) 302.
111 T.S. Glikman and L.N. Zavgorodnyaya, Biokhimiya, 38 (1973) 101.
112 L.H. Vogt, A. Zalkin and D.H. Templeton, Inorg. Chem., 6 (1967) 1725.
113 D.H. Chin, J.D. Gaudio, G.N. La Mar and A.L. Balch, J. Am. Chem. Soc., 99 (1977) 5486.
114 C.J. Weschler, B.M. Hoffman and F. Basolo, J. Am. Chem. Soc., 97 (1975) 5278.
115 B.M. Hoffman, T. Szymanski, T.G. Brown and F. Basolo, J. Am. Chem. Soc., 100 (1978) 7253.
116 A. Dedieu and M.M. Rohmer, J. Am. Chem. Soc., 99 (1977) 8050.
117 G. Porter and M.R. Wright, Discuss. Faraday Soc., 27 (1959) 18.
118 H. Linschitz and L. Pekkarinen, J. Am. Chem. Soc., 82 (1960) 2411.
119 R.G. Brown, A. Harriman and G. Porter, J. Chem. Soc. Faraday II, 73 (1977) 103.
120 M.B. Ledger and G. Porter, J. Chem. Soc. Faraday I, 68 (1972) 539.
121 I.A. Duncan, A. Harriman and G. Porter, J. Chem. Soc. Faraday II, 74 (1978) 1920
122 M.E. Bodini, L.A. Willis, T.L. Riechel and D.T. Sawyer, Inorg. Chem., 15 (1976) 11538.
123 E.J. Marshall, N.A. Philipson and M.J. Pilling, J. Chem. Soc. Faraday II, 72 (1976) 830.
124 R. Ballardini, H.F. Wasgestian, G. Varani, L. Moggi and V. Balzani, J. Phys. Chem., 77 (1973) 2614.
125 R. Ballardini, G. Varani, H.F. Wasgestian, L. Moggi and V. Balzani, J. Phys. Chem., 77 (1973) 2947.