Manganese Porphyrin Complexes. I. Synthesis and Spectroscopy of Manganese(III) Protoporphyrin IX Dimethyl Ester Halides

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Abstract: Manganese protoporphyrin IX dimethyl ester complexes of the halide ions, F^-, Cl^-, Br^-, and I^-, have been investigated. Physical and spectral properties and elemental analyses of the complexes are consistent with the formulation [Mn^{III}(porphyrin)XH_2O]. Infrared spectra of the complexes in the solid state and nonpolar solvents give evidence for coordination of the halide ions to an axial position of the metal. Visible absorption spectra support this conclusion since all the compounds show characteristic absorption in nonpolar solvents. The anion appears to be displaced in basic solvents since these spectra are anion independent. Electronic spectra of the complexes do not reproduce the normal metalloporphyrin spectrum: weak absorptions appear at ~12.5 and ~14.5 kK, moderate intensity bands appear at ~16.7 and ~17.5 kK, and strong absorptions appear at ~21.0 and ~27.0 kK. The low-energy bands are probably associated with metal–ligand charge-transfer transitions, while the high-energy bands are associated with porphyrin $\pi \rightarrow \pi^*$ transitions. The frequency order for the absorption maxima is $F^- > Cl^- > Br^- > I^-$. The relative intensity of the high-energy bands also varies appreciably with anion. The spectra and electronic structure of the complexes can be rationalized with the aid of the Gouterman molecular orbital model of metalloporphyrins. In contrast to the normal metalloporphyrins, it appears that there is significant porphyrin–metal anion π mixing in the manganese(III) porphyrin complexes.

Manganese has been implicated in oxygen formation which occurs during green plant photosynthesis.[1] In fact, two manganese ions are found per photosynthetic unit in the chloroplast.[2] Several suggestions have been made as to the function of the manganese ion in the liberation of oxygen by photosystem II. In these schemes the Mn(II)–Mn(III)–Mn(IV) redox system is thought to take part in the electron-transfer chain from an electron donor to an electron acceptor.[3] Unfortunately the metal atom binding sites and the ligands at these sites are not known. Calvin has suggested that a relevant model for the manganese in the chloroplast would be manganese complexes of porphyrin-like ligands.[4] The photochemical and redox behavior of phthalocyanine,[5] porphyrin,[6] and chlorophyll[7] complexes of manganese have been extensively investigated. These studies have concentrated on delineating the redox properties of the compounds in aqueous solution, with the purpose of using this information to understand the mechanism and energetics of the role the metal ion plays in photosynthesis. In this work the structural aspects of the materials were not emphasized.

As a basis to understanding the chemistry of manganese porphyrins in general, and their possible role in photosynthesis in particular, we have undertaken a study of the synthesis and spectroscopy of manganese porphyrin complexes. In this paper, we report some results for the halide complexes of manganese(III) protoporphyrin IX dimethyl ester. A structural representation of the compounds is given in Figure 1.

The preparation and properties of some manganese porphyrins have been previously reported. A manganese(III) porphyrin was first prepared by Zaleski.[8] This mesoporphyrin IX complex was not fully investigated until sometime later when Taylor examined its redox properties.[9] In the same study the electronic absorption spectra were given for the first time. In addition, the following porphyrin complexes have been reported: (acetato)etioporphyrin II,[5] (acetato)hematoporphyrin IX dimethyl ester, and (chloro)hematoporphyrin IX dimethyl ester.[6] The spectroscopy of these materials has not been examined in detail. The complexes shown in Figure 1 are reported here for the first time.

Experimental Section

Materials. Protoporphyrin IX dimethyl ester (purity >95%) was obtained from Sigma Chemical Co. and used without further purification. All other materials were reagent grade and solvents were spectrograde. Chloroform was washed with water to remove ethanol, dried over Drierite, and used immediately.

The complexes were synthesized by the same general procedure: 500 mg (8.5×10^{-4} mole) of protoporphyrin IX dimethyl ester and 500 mg (2.0×10^{-3} mole) of manganese acetate tetrahydrate are refluxed in 75 ml of glacial acetic acid for 4 hr. No attempt is made to exclude air or shield the reaction mixture from light. After cooling, the reaction mixture is reduced to a volume of less than 5 ml. The resulting sludge is then extracted with 1000 ml of distilled water at 50°. A 200-ml portion of a 1 *N* solution of the appropriate sodium halide is then added to the filtrate. The resulting mixture is stirred, at room temperature, for 15 min. A red-brown precipitate is collected on a Büchner funnel, washed with a little water, and air-dried. The residue is then extracted with 500 ml of benzene in a Soxhlet flask. The benzene solution is reduced to a volume of 25 ml and then cooled. The precipitate that forms is collected on a Büchner funnel, washed with petroleum ether, and air-dried. The dark red powder is then dried at 105° over P_2O_5 *in vacuo*, yield ~200 mg (~35%). An alternate method of purification of the original precipitate involves extraction with hot water and reprecipitation with aqueous sodium halide. This procedure does not result in an increase in the purity of the product

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[2] R. B. Park and N. G. Pon, *J. Mol. Biol.*, 6, 105 (1963).

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[6] P. A. Loach and M. Calvin, *Biochemistry*, 2, 361 (1963).

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Table I. Elemental Analysis for [Mn(DMPrpor)XH$_2$O]

Empirical formula	Mol wt	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	%Mn Calcd	%Mn Found	%X Calcd	%X Found
$C_{36}H_{36}O_4N_4MnF \cdot H_2O$	680.7	63.52	63.64	5.63	5.40	8.23	8.46	8.07	8.17	2.79	1.99
$C_{36}H_{36}O_4N_4MnCl \cdot H_2O$	697.1	62.02	62.43	5.49	5.23	8.04	7.91	7.88	8.01	5.09	5.37
$C_{36}H_{36}O_4N_4MnBr \cdot H_2O$	741.6	58.31	58.48	5.16	5.27	7.56	8.01	7.41	7.94	10.78	10.86
$C_{36}H_{36}O_4N_4MnI \cdot H_2O$	788.6	54.83	55.64	4.86	4.76	7.10	6.96	6.97	6.45	16.09	16.42

(although the yield is decreased). Similarly, chromatography on alumina leads to some decomposition of the complex.

Spectral Measurements. The spectra, in the 4000–650-cm^{-1} region, were obtained with the materials dispersed in a potassium bromide disk and were checked with mineral oil mulls with a Beckman IR-12 grating infrared spectrophotometer. Solution spectra, usually in methylene chloride and chloroform, were also obtained. A Perkin-Elmer No. 301 double-beam grating spectrophotometer (with a dry nitrogen purge) was used to study the 650–160 cm^{-1} region. Spectra were obtained with concentrated mineral oil mulls of the materials placed between thin disks of high density polyethylene. Two disks of polyethylene were also placed in the reference beam. Frequencies quoted for the ir could be reproduced to at least ± 4 cm^{-1}. Absorption spectra were recorded with a Cary Model 14 spectrophotometer with multiple benzene, chloroform, methanol, and pyridine solutions ($1\text{–}10 \times 10^{-5}$ *M*) of the materials in matched silica cells. Generally, the path length was 5 cm in the 1000–600-mμ range, 1 cm in the 700–500-mμ range, and 0.2 cm in the 500–300-mμ range. The position of the broad absorption maxima could be reproduced to better than ± 0.1 kK. Magnetic susceptibility measurements at 23° were carried out with Faraday balance using platinum metal as a standard. The diamagnetic correction for protoporphyrin IX dimethyl ester was taken to be 330×10^{-6} cgs.[6] Multiple readings were taken at two different field strengths. The magnetic moments agreed to within ± 0.1 BM.

Results and Discussion

Synthesis. Manganese(III) porphyrin complexes can be prepared by making use of the standard metalloporphyrin synthesis;[10] *i.e.*, a mixture of the divalent metal acetate and porphyrin is refluxed in glacial acetic acid. In the presence of air, the manganese(II) porphyrin is rapidly oxidized to the +3 oxidation state. The over-all reaction is given by

$$\mathrm{Mn(solv)_6}^{2+} + \mathrm{H_2(DMPrpor)} \xrightarrow{[\mathrm{O_2}]} [\mathrm{Mn(DMPrpor)solv_2}]^+ + 2\mathrm{H}^+ + 4\mathrm{solv} \quad (1)$$

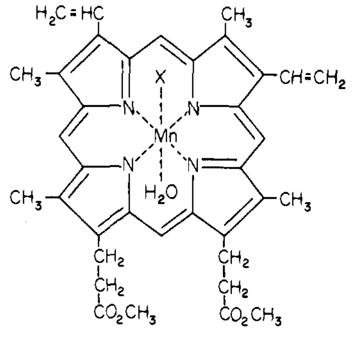
where solv represents the solvent molecule, glacial acetic acid. Under the usual laboratory conditions, and even with the routine exclusion of air, the manganese(III) porphyrin is the most stable complex formed. The +2 oxidation state, however, can be obtained by the reduction of the manganese(III) porphyrin with sodium dithionate.[6] Removal of the solvent in reaction 1 leads to the formation of acetato(acetic acid)manganese(III) porphyrin. After dissolutions of this material in water, the halide complex is precipitated from solution by addition of a 100-fold excess of sodium halide. On the other hand, addition of a solution of sodium nitrate, phosphate, and sulfate does not result in precipitate formation (eq 2).

$$[\mathrm{Mn(DMPrpor)(H_2O)_2}]^+ + \mathrm{X}^- \rightleftharpoons [\mathrm{Mn(DMPrpor)XH_2O}] + \mathrm{H_2O} \quad (2)$$

The ease of precipitation of the complex follows the order $\mathrm{I}^- > \mathrm{Br}^- > \mathrm{Cl}^- > \mathrm{F}^-$. As expected, the solubility in water follows the reverse of this order. The halide complexes are readily soluble in pyridine (py), methanol, and other coordinating (basic) solvents, presumably giving rise to the disolvo complex with the liberation of halide ion.[11]

$$[\mathrm{Mn(DMPrpor)XH_2O}] + 2\mathrm{py} \rightleftharpoons [\mathrm{Mn(DMPrpor)(py)_2}]^+ + \mathrm{H_2O} + \mathrm{X}^- \quad (3)$$

The materials are also soluble in chloroform and somewhat less soluble in benzene and the other nonpolar solvents. Pyridine, methanol, chloroform, and benzene solutions appear to be stable at room temperature for days; *i.e.*, the electronic absorption spectra of the compounds are identical before and after standing for 1 week. No attempt was made to shield the solutions from light or to exclude oxygen. It thus appears that the manganese(III) complexes are oxidatively and photolytically stable in nonaqueous solution (under the conditions stated) and presumably also in the solid state. In addition, the absorption maxima and intensity are independent of concentration in the $10^{-3}\text{–}10^{-6}$ *M* range for the manganese(III) porphyrin in methanol,[7] chloroform,[7] and also benzene. This suggests that only one state of aggregation exists in these solutions. In fact, molecular weight measurements for the (chloro)-hematoporphyrin complex indicate that the material is in the monomeric state.[7]



Mn(DMPrpor)XH$_2$O

Figure 1. Structural representation of aquo(halo)manganese(III) protoporphyrin IX dimethyl ester: X = F$^-$, Cl$^-$, Br$^-$, I$^-$.

The materials formed by reaction 2 are powdery red-brown solids. The solids do not show a defined melting point below 300°, but slowly darken and become black around 250°. Elemental analyses are given in Table I.[12] Considering the complexity of the materials, the data are in excellent agreement with the theoretical values. It appears that approximately one molecule of water is associated with each complex. This water is tightly bound since it is not removed by extended drying at 105° *in vacuo*.

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(10) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964, p 125.

(11) P. E. Hambright, *Chem. Commun.*, 470 (1967).

(12) Elemental analyses performed by Galbraith Laboratories, Knoxville, Tenn., and Crobaugh Laboratories, Charleston, W. Va.

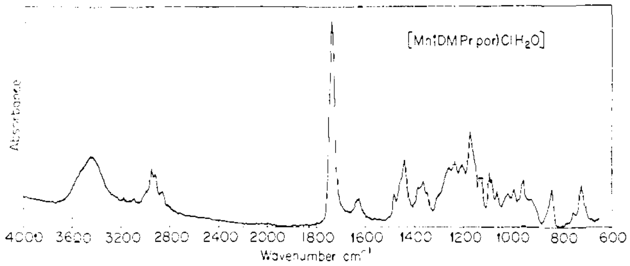

Figure 2. Infrared absorption spectrum, 4000–650 cm^{-1}, of aquo(chloro)manganese(III) protoporphyrin IX dimethyl ester in a potassium bromide disk.

Magnetic susceptibility measurements were made on the solid complexes. The effective magnetic moments (Bohr magnetons) are 4.80 for F$^-$, 4.97 for Cl$^-$, 4.87 for Br$^-$, and 4.86 for I$^-$. The magnetic moments lie in the range 4.8–5.0 BM, which corresponds to the spin-only value for four unpaired electrons, 4.9 BM. This agrees with the expected value for the spin-free d^4, manganese(III) case. Other common oxidation states of the metal could not contain four unpaired electrons; *i.e.*, the +2 oxidation state would have one, three, or five while the +4 state would have one or three unpaired electrons. The susceptibility measurements reported here were only taken at one temperature, 23°. On the other hand, Loach and Calvin have determined the susceptibility at a number of temperatures for the (chloroaquo)manganese(III) hematoporphyrin IX dimethyl ester. The complex adheres to the Curie law (the Weiss constant equal to zero).[6] The complexes also show the same magnetic moments in the solid state and in aqueous pyridine solution.

Infrared Spectra. Infrared spectra in the 4000–650-cm^{-1} range were determined with the complexes in the solid state and in solution. A representative solid-state spectrum is shown in Figure 2. The frequencies and relative intensities of the absorption maxima in the rock salt region were, within experimental error, identical for all the complexes in the solid state as well as in solution. In addition, the spectra closely resemble those found previously for the divalent metalloporphyrins.[13] In fact, the metal-independent infrared absorptions can be assigned with the aid of the group frequency correlations derived in that work. For example, medium weak bands at 2950, 2930, and 2870 cm^{-1} are associated with the antisymmetric and symmetric alkyl C–H vibrations. Very weak vinyl C–H stretching absorptions at 3090 and 3010 cm^{-1} are also noted. The alkyl C–H antisymmetric deformations give rise to medium intensity absorption peaks at 1438 and 1380 cm^{-1}. Characteristic vinyl C–H bending modes absorb at 992 and 927 cm^{-1}. A sharp peak at 840 cm^{-1} can be assigned to the methine C–H bend. The strongest absorption peak in the spectra, at 1736 cm^{-1}, can be assigned to the methyl propionate ester carbonyl stretch. Finally, the ester carbon–oxygen "single bond" stretching vibration gives rise to a strong absorption at ~1170 cm^{-1}.

The C=C, C=N stretching vibration of the porphyrin macrocycle should give rise to a number of absorptions in the 1500–1700-cm^{-1} range. In fact, only one broad medium weak absorption, at 1622 cm^{-1}, is resolved in this region in the solid-state spectrum. Among others, this peak may be associated with the vinyl group stretch or the coordinated water bending mode. Solution spectra show weak absorptions at 1680, 1621, 1600, and 1580 cm^{-1}. The spectra strongly resemble those of the zinc and magnesium porphyrins. In contrast to the weak absorptions noted here for the 1500–1700-cm^{-1} region, chlorins (reduced porphyrins) show medium-strong bands in this region.[14] Metal-independent absorptions at 1360 and 1232 cm^{-1} can be assigned to the breathing and out-of-plane deformations of the porphyrin ligand.

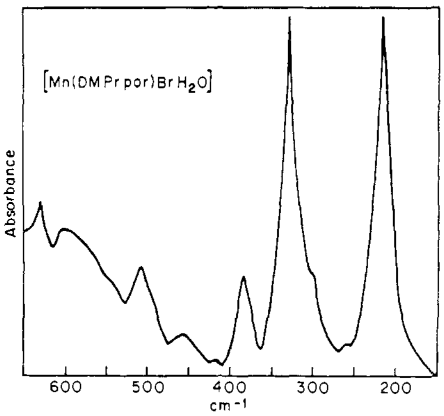

Figure 3. Infrared absorption spectrum, 650–160 cm^{-1}, of aquo(bromo)manganese(III) protoporphyrin IX dimethyl ester in a Nujol mull.

Spectra in the 650–160-cm^{-1} region were determined with the complexes in the solid state. A typical spectrum is given in Figure 3. The absorption peaks shown are one-fifth the intensity of those in the rock salt region. In contrast to the near identity of the rock salt spectra, the low-frequency spectra are characteristic for each complex. The most prominent absorption in this region appears at 462 cm^{-1} for F$^-$, 262 cm^{-1} for Cl$^-$, 211 cm^{-1} for Br$^-$, and 190 cm^{-1} for I$^-$. These absorptions do not appear in the spectra of the divalent metalloporphyrins. It seems reasonable to assign these bands to the manganese–halogen stretching vibration. The frequency of the peaks show the expected decrease with the increasing mass of the halogen. The absorptions noted here are also in the range observed for manganese(II) and manganese(III) halide complexes,[15] *i.e.*, ν(Mn–F) ~ 407–560 cm^{-1}, ν(Mn–Cl) ~ 284 cm^{-1}, ν(Mn–Br) ~ 219 cm^{-1}, and ν(Mn–I) ~ 185 cm^{-1}. In addition to the halide-dependent absorption, there are a number of other prominent absorptions in the low-frequency spectrum. These bands are common to all the manganese(III) porphyrins as well as to the divalent metalloporphyrins.[15] For example, the methyl propionate ester deformations appear at 640, 610, and 440 cm^{-1}. Prominent absorptions at 382 and 332 cm^{-1} can be associated with the porphyrin macrocycle deformation modes. The frequency of the latter absorption is markedly lower (~20 cm^{-1}) than for divalent metalloporphyrins. A metal-dependent porphyrin deformation absorption appears at ~510 cm^{-1}

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(14) L. J. Boucher and J. J. Katz, *ibid.*, **89**, 4703 (1967).

(15) A. Sabatini and L. Sacconi, *ibid.*, **86**, 17 (1964); R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959); J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1305 (1965).

for all the manganese porphyrin complexes. The frequency of this band as well as the metal-dependent porphyrin band at 953 cm^{-1} places manganese(III) halide in the order: Pd > Co > Ni > MnX > Cu > Ag > Zn > Ag > Cd. It has been suggested that the frequency order is directly related to the strength of the metal–porphyrin interaction.[13]

The infrared spectra of the manganese(III) porphyrin complexes are entirely consistent with the structural representation given in Figure 1. The rock salt region spectra give no evidence for alteration of the side chains or of the porphyrin macrocycle. The low-frequency spectra are consistent with the notion of a strongly bound anion coordinated to the manganese atom. Whether or not a water molecule is coordinately bound is somewhat more difficult to assess. The solid-state spectra do, however, show prominent absorptions that, at 3450 and 1620 cm^{-1}, might be assigned to coordinated water vibrations. It must be admitted that potassium bromide disks always show absorbed water regardless of sample. The chloroform solution spectra, however, do show weak water bands at 3440 and 1620 cm^{-1}.

Electronic Spectra. The visible absorption spectra of the halide complexes of the manganese(III) porphyrin were measured in the 10–30-kK region. The positions of the absorption maxima for benzene and chloroform solutions are given in Table II. Typical electronic spectra are shown in Figure 4. In general, the spectra consist of at least six prominent absorptions, designated bands I to VI. The two low-intensity bands I and II ($\epsilon \sim 1 \times 10^3$) appear in the near-infrared region at ~12.5 and ~14.5 kK. A somewhat higher intensity band, IV ($\epsilon \sim 1 \times 10^4$), is seen at 17.5 kK. A resolvable shoulder appears to the red side of this band at approximately 16.7 kK. Finally the two most intense bands, V and VI ($\epsilon \sim 5\text{–}10 \times 10^4$), appear around 21.0 and 27.0 kK, in the near-ultraviolet. There is also a prominent shoulder on the blue side of band V at ~20.9 kK for the iodide complexes. The spectral pattern is the same for the benzene and chloroform solutions. Some of the maxima are sharpened and red shifted (0.1–0.2 kK) in going from benzene to chloroform. However, only bands I and II appear to be significantly shifted by the change in solvent. The solvent effect may be related to the hydrogen-bonding ability of the chloroform. The low-energy charge-transfer bands of manganese(III) β-diketone complexes have been observed to shift in going from benzene to chloroform solutions.[16] In benzene solution the frequency order for the complexes is F$^-$ > Cl$^-$ > Br$^-$ > I$^-$. Although all the absorption maxima vary in the same way, the high-energy bands show a significantly larger anion dependence.

Table II. Visible Absorption Maxima (kK[a]) for [Mn(DMPrpor)XH$_2$O] Complexes

Band	Solvent	X: F	Cl	Br	I
I	Chloroform	12.7	12.7	12.6	12.4
II		14.6	14.6	14.4	14.3
III		16.8[b]	16.7[b]	16.7[b]	. . .
IV		17.7	17.6	17.5	17.3
V		21.0	20.9	20.7	19.8
VI		27.3	27.2	27.0	26.5
R (V/VI)		0.74	0.74	0.50	0.28
I	Benzene	12.9	12.9	12.8	12.5
II		14.9	14.7	14.6	14.5
III		16.8[b]	16.7[b]	16.6[b]	. . .
IV		17.7	17.5	17.4	17.4
V		21.0	20.9	20.6	19.8
VI		27.3	27.2	27.0	26.5
R (V/VI)		0.67	0.73	0.49	0.28

[a] kK (kilokaiser) = 1000 cm^{-1}. [b] Shoulder.

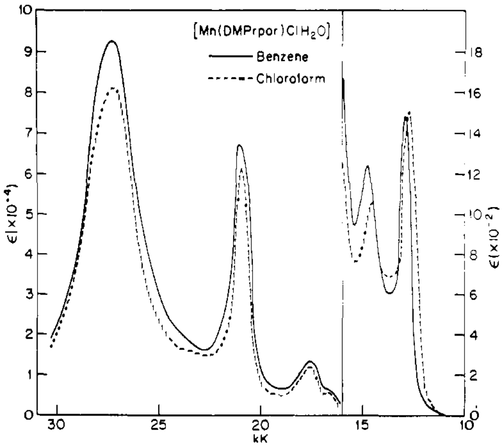

Figure 4. Visible absorption spectra of aquo(chloro)manganese(III) protoporphyrin IX dimethyl ester.

A striking feature of the electronic spectra of the manganese(III) porphyrin complexes is the occurrence of two low-energy bands of modest intensity in the near-infrared. It is interesting to note that divalent and trivalent metalloporphyrins (including manganese(II)) do not show these absorptions. It is possible that bands I and II arise from ligand field transitions of the manganese(III) ion. The intensity of the absorptions is an order of magnitude higher than observed for normal ligand field bands. However, the intensity of the absorptions is in the range expected for charge-transfer bands. In fact, simple manganese(III) chelates usually show low-energy metal–ligand charge-transfer bands.[17] Further, the positions of the low-energy bands only vary slightly with anion.

The assignment of bands III and IV is also somewhat uncertain. The intensity of this peak is about one-sixth that of the porphyrin $\pi \rightarrow \pi^*$ transitions. The anion dependence of bands III and IV is about the same as for bands I and II. A reasonable assignment of this band would be to one (more) of the many allowed ligand–metal charge-transfer transitions.

Typical visible absorption spectra of metalloporphyrins consist of two prominent bands, α and β, in the 16–20-kK region ($\epsilon \sim 1 \times 10^4$) and a third more intense band, Soret ($\epsilon \sim 2 \times 10^5$), at 23–25 kK. The visible absorption bands have been assigned to $\pi \rightarrow \pi^*$ transitions of the porphyrin macrocycle. The $a_{2u}(\pi) \rightarrow e_g{}^*(\pi)$ and $a_{1u}(\pi) \rightarrow e_g{}^*(\pi)$ transitions are near degenerate in energy and are mixed because of electron interaction.[18] The resultant excited states are a low-energy *Q* state (α, β) in which the transition dipoles nearly cancel (low intensity) and higher energy B state (Soret) in which the transition dipoles add (high intensity). It

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(16) J. P. Fackler, T. S. Davis, and I. D. Chavlo, *Inorg. Chem.*, **4**, 132 (1965).

(17) R. Dingle, *Acta Chem. Scand.*, **20**, 33 (1964).

(18) C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectry.*, **16**, 415 (1965).

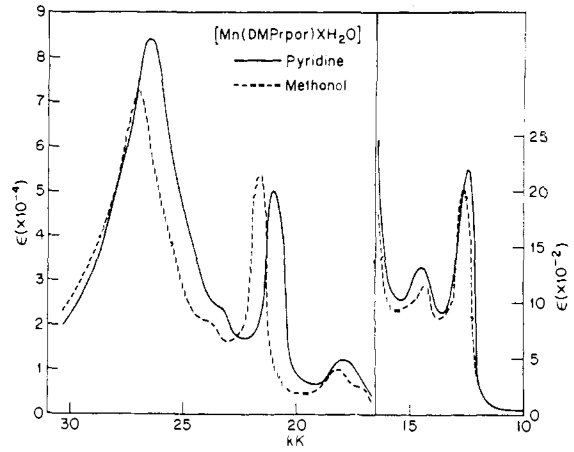

Figure 5. Visible absorption spectra of aquo(halo)manganese(III) protoporphyrin IX dimethyl ester: X = F^-, Cl^-, Br^-, I^-.

has been concluded from the observed spectral patterns and molecular orbital calculations that the metal and porphyrin π systems are only weakly interacting.[19] Since there appears to be no appreciable ligand–metal π bonding for the divalent metalloporphyrin (including Mn(II)), the degeneracy of the filled π levels, $a_{1u}(\pi)$ and $a_{2u}(\pi)$, is not removed. The average energy of the *B* and *Q* bands is about 21 kK for all metalloporphyrins.

The electronic spectra of the manganese(III) porphyrin complexes are considerably different from those of the divalent metalloporphyrins. The +3 oxidation state of the metal is not necessarily related to this difference since the corresponding cobalt and iron complexes show normal spectra.[20,21] For the manganese(III) complexes the Soret band appears to be split into two near-equal intensity bands at ~27.0 and ~21.0 kK. It is interesting to note that band V appears at approximately the average energy of the *B* and *Q* bands of the normal metalloporphyrin spectrum. Of the two highest filled π orbitals of the porphyrin, only the $a_{2u}(\pi)$ can effectively overlap with the metal π orbitals. Significant π mixing of the metal ion and porphyrin levels could result in the partial lifting of the accidental degeneracy of the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ levels. The interaction of the filled $a_{2u}(\pi)$ level with the partially filled d levels would be bonding with respect to the porphyrin orbital. Therefore the energy of the level should be lowered. In the absence of mixing of the porphyrin π levels together (caused by electron interaction), the $a_{2u}(\pi)$ and $a_{1u}(\pi)$ to $e_g{}^*$ transitions should be of near-equal intensity and occur at different energies. For example, the $a_{1u}(\pi) \rightarrow e_g{}^*$ transition should be of low energy and should appear near the average of mixed *B* and *Q* bands. The $a_{2u}(\pi) \rightarrow e_g{}^*$ transition would then be of higher energy, perhaps above the original Soret band. It is suggested that bands V and VI observed here for the manganese(III) porphyrins correspond to these transitions.

The positions of both bands V and VI vary with the anion bound to the metal. The ligand-to-metal π interaction would be antibonding with respect to the metal d orbitals. The extent to which this interaction takes place with the porphyrin π system depends on the extent of the π mixing of the metal with axial anion ligand.

If the degeneracy of the a_{1u} and a_{2u} levels is removed by the porphyrin-to-metal interaction, then the mixing of the two π levels by electron interaction would be, of course, lessened. In the limit the $a_{1u}(\pi) \rightarrow e_g{}^*(\pi)$ transition should not be markedly dependent on the anion bound to the metal in the axial coordination position. In fact, band V is just as dependent on the anion, and in the same way, as band VI. This observation supports the notion that the porphyrin π levels are still mixing together and that this also is anion dependent. The relative intensities of the two bands (V, VI) are consistent with this. While the relative intensities of bands I, II, III, and IV remain essentially constant for all the anion complexes, the relative intensities of bands V and VI do vary appreciably. For the fluoride complexes the ratio of the two bands *R* (V/VI) is ~0.7, while for the iodide complex the intensity ratio is ~0.3. The difference in the relative intensities for bands V and VI arises *via* an intensity robbing from band V by band VI. Relative to band IV, band V decreases in intensity, and band VI increases in intensity in going from the fluoride to the iodide complex. The mechanism of the intensity borrowing is probably the same as that proposed for the *B* and *Q* bands of the normal metalloporphyrin spectrum.

Since the spectra are different for each of the halide complexes of manganese(III) porphyrin in benzene and chloroform, it is reasonable to assume that the anions are coordinately bound to the manganese atom in these solvents. On the other hand, when each of the complexes is dissolved in a good coordinating solvent such as pyridine or methanol, the spectra are all identical with each other. Table III lists the positions of the absorption maxima of the complexes in pyridine and methanol solution. Typical electronic spectra are shown in Figure 5. The spectra are different for the two solvents and are also different from those of the anion complexes. Band II also appears to be split into two components, A and B. The spectral data indicate that the same species is present in each of the solvents, *i.e.*, the disolvo complexes. The equilibrium operative here is shown in reaction 3. All the absorptions are at lower energy for the pyridine solutions than for the methanol solutions. In fact, the pyridine values correspond roughly to between those of the bromide and iodide complex in benzene. An exception to this is the position of band V which is at higher energy than for any of the halide complexes. The relative intensity of bands V and VI also places pyridine near the bromide ion in the ligand series. The absorption maxima for

Table III. Visible Absorption Maxima (kK[a]) for [Mn(DMPrpor)XH$_2$O]

Band	Methanol	Pyridine
I	12.6	12.4
IIA	14.4	14.2
IIB	14.8	14.5
III	17.2[b]	17.1[b]
IV	18.2	18.0
V	21.6	21.0
VI	27.0	26.5
R (V/VI)	0.75	0.59

[a] kK (kilokaiser) = 1000 cm^{-1}. [b] Shoulder.

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the complexes in methanol are at the high-energy end of the ligand series, *i.e.*, close to those of the fluoride complexes. The value of R (V/VI) is also consistent with this position.

The exact nature of the porphyrin–metal d-orbital π interaction is difficult to describe since the structure of the complexes is unknown. One possibility is a tetragonal geometry with the metal atom in the plane of the four porphyrin nitrogen donors and the axial anion and solvent molecules at a somewhat larger distance from the metal. If a water molecule is not bound to the metal, then the geometry would be square pyramidal. For either of these arrangements the d_{xz}, d_{yz} orbitals would be of proper symmetry for overlap with the porphyrin-filled π orbitals. The d_{xz}, d_{yz} pair can also interact with the filled π orbitals on the axial anion. Competition for this orbital then could give rise to the observed anion dependence of the porphyrin $\pi \rightarrow \pi^*$ transition. It must be admitted, however, that the porphyrin interaction must be the more important of the two. The anion dependence is, after all, only a small perturbation on the manganese(III) porphyrin spectrum.

Another likely choice for the geometry of the manganese(III) porphyrin complex would be one in which the metal atom was out of the plane of the porphyrin and closer to the axial anion. The solvent molecule would then be weakly bound (if at all) to the metal in the axial position on the opposite side of the metal. This situation is in fact observed for the iron(III) porphyrin complexes.[22] In this case the separation of the d orbitals into σ and π bonding sets is not straightforward. For example, the d_{z^2} orbital can now mix into the filled $a_{2u}(\pi)$ orbital of the porphyrin.[20] Since the metal orbital is involved in bonding to the axial anion, some anion character can be entered into the $a_{2u}(\pi)$ porphyrin orbital.

The unusual porphyrin–manganese interaction suggested here is manifest in several other properties of the complexes. The materials are photochemically active, being reduced by visible light in the absence of air.[5,6] The presence of visible charge-transfer bands in the near-infrared provides a convenient route for the photoreduction of the complexes. Many simple manganese(III) complexes are photoactive, presumably for the same reason.[23] The absorption spectra indicate that the electronic structure of the metalloporphyrin is dependent on the anion (ligand) bound to the metal in the axial coordination positions. It seems reasonable to assume that the photochemical properties and redox potentials will also be dependent on these ligands.

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Hydrogen-1 Nuclear Magnetic Resonance Studies of the Formation and Decarbonylation of Diphosphine-Substituted Acetylmanganese Tricarbonyl Complexes

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Abstract: The reactions of a number of phosphorus donor ligands, L, with *cis*-$CH_3Mn(CO)_4L$ or *cis*-$CH_3COMn(CO)_4L$ were observed to fall into three categories: (1) when L is $P(OCH_2)_3CCH_3$ or $P(C_6H_5)_2H$, the exclusive product is 2,3-L_2-1-$CH_3COMn(CO)_3$ (facial); (2) for L equal to $P(C_6H_5)_2CH_3$, $P(OC_6H_5)_3$, or $P(C_2H_5)_3$, the only product observed is 2,4-L_2-1-$CH_3COMn(CO_3)$ (meridional *trans*-L_2); (3) the ligands $P(C_6H_5)(CH_3)_2$ and $P(OCH_3)_3$ were seen to yield facial complexes which rearranged rapidly to the meridional structure. These variations in products are explained in terms of L–L and L–acetyl steric interaction as the facial isomer is thermodynamically favored when L is relatively small and the meridional isomer is preferred when L has more stringent spacial requirements. Each meridional acetylmanganese complex, but not the facial complexes, was decarbonylated to 2,4-L_2-1-$CH_3Mn(CO)_3$. Structural assignments are based on infrared and ^1H nmr spectral observations and on dipole moments in selected cases.

Most of the investigations on the reactions of methylmanganese pentacarbonyl with Lewis bases have dealt with the formation of *cis*- and *trans*-$CH_3COMn(CO)_4L$ complexes and their subsequent decarbonylation to *cis*-$CH_3Mn(CO)_4L$ complexes.[2] However, there are two literature reports on the direct formation of $CH_3COMn(CO)_3L_2$ complexes from $CH_3Mn(CO)_5$ and L, where L is $(C_6H_5O)_3P_3$, $(C_6H_5O)_2PCH_3$,[3] or the chelating ligand $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.[3,4]

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