Manganese Porphyrin Complexes. III. Spectroscopy of Chloroaquo Complexes of Several Porphyrins

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Abstract: Chloro(aquo)porphyrinmanganese(III) complexes have been synthesized and characterized for a number of different porphyrins, including etioporphyrin I, deuteroporphyrin IX dimethyl ester, mesoporphyrin IX dimethyl ester, hematoporphyrin IX dimethyl ester, protoporphyrin IX dimethyl ester, $\alpha,\beta,\gamma,\delta$-tetraphenylporphin, and methyl pheophorbide a. The absorption spectra have been recorded with the complexes in chloroform and pyridine solution. All the porphyrins show the several features typical of manganese(III) porphyrins, *i.e.*, weak near-ir bands, an intense extra absorption around 21.0 kK, and a blue-shifted B band. All the maxima are red-shifted as the donor strength of the macrocycle decreases from etioporphyrin to methyl pheophorbide a. A model for manganese(III) porphyrins is proposed and a tentative assignment of the absorption spectra of all the complexes made. The near-ir bands and extra absorption are assigned to porphyrin-to-manganese charge-transfer bands while other prominent absorptions are assigned to the normal Q and B bands. The intense charge-transfer bands and the blue-shifted B band can be rationalized by invoking strong metal $d\pi \rightarrow$ porphyrin $e_g{}^*$ mixing.

Porphyrinmanganese(III) complexes are of considerable interest for several reasons. For one, the unique absorption spectrum of these materials is presumably diagnostic of an unusual electronic structure.[1] A thorough understanding of the manganese porphyrins would be valuable in sorting out the closely related and biologically important iron system[2] as well as for the general understanding of metalloporphyrin spectra and structure.[3] A second reason is the relevance of the porphyrin complexes as model compounds for the manganese-dependent oxygen evolution in green plant photosynthesis.[4]

A study of the effect of axial anions and other donors as well as solvents on the properties of a porphyrin-manganese complex has been reported.[5] As an extension of this work, we have synthesized and examined a series of manganese complexes in which the porphyrin is varied. A structural representation of the materials is given in Figure 1. A study of these complexes should allow the assessment of the influence of the in-plane macrocycle on the chemical and physical properties of the manganese complexes.

Experimental Section

Materials. Hematoporphyrin IX dimethyl ester was prepared from hematoporphyrin IX dihydrochloride (Pierce Chemical Co.) according to the procedure of Loach and Calvin.[6] Etioporphyrin I was synthesized by the method of Erdman and coworkers.[7] Methylpheophorbide a was obtained from pheophytin a and b (Fluka A. G. Chemische Fabrik) by the method of Willstätter and Stoll.[8] The remaining porphyrins were obtained commercially and used without further purification: protoporphyrin IX dimethyl ester (Sigma Chemical Co.), deuteroporphyrin IX dimethyl ester (Koch Light Laboratories), mesoporphyrin IX dimethyl ester (Pierce Chemical Co.), $\alpha,\beta,\gamma,\delta$-tetraphenylporphin (Mad River Chemical Co.). The porphyrinmanganese complexes were prepared and purified according to the procedure set out in a previous paper.[1] The purity of the materials was confirmed by elemental analyses (C, H, N, Mn, Cl) and by thin-layer chromatography.

Spectral Measurements. The magnetic moments and uv-visible and ir spectra were determined as previously described.[1] The magnetic circular dichroism spectra were obtained with a Durram-Jasco spectropolarimeter equipped with a 65-kG magnet. The spectra were obtained with dilute chloroform solutions at room temperature.

Results

The chloride complexes of the manganese(III) porphyrins were studied because of the relative ease of preparation of these materials in a high state of purity. Several of these complexes have been previously reported.[6,9] Many other anion complexes were also prepared. Except for the expected axial-anion-dependent spectral shifts, their properties were analogous to the chloro complexes. Magnetic susceptibility measurements at room temperature gave values of the effective magnetic moments in the range 4.8–5.0 BM for all the complexes. This is consistent with a high-spin d^4 configuration. The rock salt infrared spectra of the materials are consistent with the assumed structure and do not indicate any alteration of the macrocycle.[10,11] The far-infrared spectra showed the usual macrocycle deformation[10] bands and the axial ν(Mn–Cl) stretching band in the 260–280-cm^{-1} range. The position of the maximum is variable but does not appear to vary in a regular way, *e.g.*, with the basicity of the porphyrin.

The near-ir and visible absorption spectra of the complexes were determined for both chloroform and pyridine solutions. Detailed spectra of these materials are presented here for the first time. In the case of the pyridine solution, the axial coordination positions of the complexes are assumed to be occupied by the solvent

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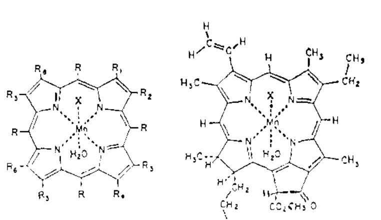
Table I. Absorption Maxima (kK) of $[Mn(por)ClH_2O]$ in Chloroform

Band	Porphyrin						
	Etio	DMMepor	DMDepor	DMHpor	DMPrpor	TPP	Me pheo a
I	12.8[a]	12.7	12.9	12.8	12.7	13.0	9.9
II	14.5[a]	14.6	14.6	14.6	14.6	~14.5	11.5
III	16.9[a]	16.9	17.0	16.9	16.7	16.2	~18.2
IV	17.9[a]	17.8	17.9	17.7	17.6	17.2 19.0	14.6
V	21.1[a]	21.1	21.2	21.0	20.9	20.9	21.3
V_a	~23.4	~23.3	~23.6	~23.4	~23.3	~25.0	22.7
VI	28.1[b]	27.9	28.4	27.9	27.6	26.7	27.2
R(V/VI)	0.69	0.73	0.85	0.79	0.75	1.76	0.53

[a] ±0.1 kK. [b] ±0.2 kK.

molecule while in chloroform these positions are filled by the chloride ion and water molecule.[5] Typical spectra are shown in Figures 2, 3, and 4. The positions of the absorption maxima are collected in Tables I and II, along with the ratios of the intensities of bands V and VI. The spectra of the five porphyrin complexes in Table I are very similar to that of protoporphyrin IX dimethyl ester. The complexes give typical manganese(III) spectra with two near-ir bands, I and II, and bands III and IV in the 15.0–18.0-kK range and two intense



Compound		Substituents[a]								
		R	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
Deuteroporphyrin IX dimethyl ester	DMDepor	H	M	H	M	H	M	PrM	PrM	M
Mesoporphyrin IX dimethyl ester	DMMesopor	H	M	E	M	E	M	PrM	PrM	M
Hematoporphyrin IX dimethyl ester	DMHpor	H	M	ME	M	ME	M	PrM	PrM	M
Protoporphyrin IX dimethyl ester	DMPrpor	H	M	V	M	V	M	PrM	PrM	M
Etioporphyrin I	Etio	H	M	E	M	E	M	E	M	E
Tetraphenylporphin	TPP	Ph	H	H	H	H	H	H	H	H
Pheophorbide a monomethyl ester	$MePheo_a$	Figure on right								

[a] M = CH_3; E = CH_2CH_3; V = $CH{=}CH_2$; ME = $CHOHCH_3$; PrM = $CH_2CH_2CO_2CH_3$; Ph = C_6H_5

Figure 1. Structural representation of porphyrinmanganese complexes.

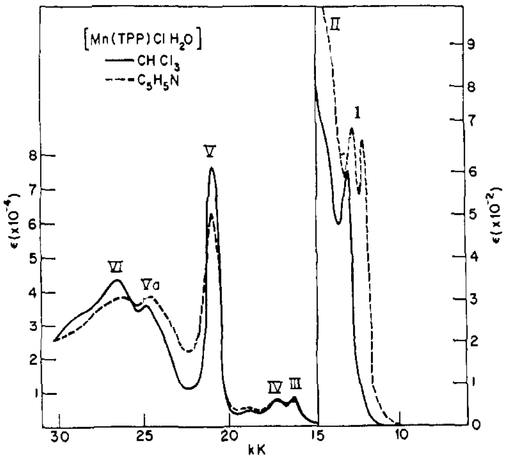


Figure 2. Visible absorption spectra of aquo(chloro)tetraphenylporphinmanganese(III).

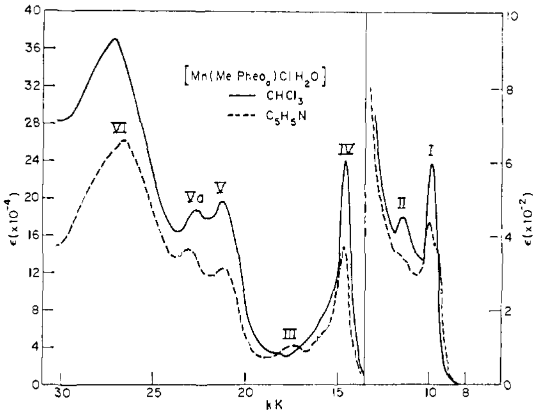


Figure 3. Visible absorption spectra of aquo(chloro)(methylpheophorbide a)manganese(III).

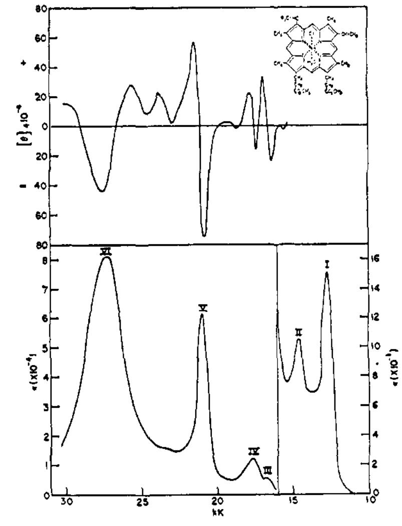


Figure 4. Visible and magnetic circular dichroism spectra of aquo(chloro)(protoporphyrin IX dimethyl ester)manganese(III) in chloroform (at 65 kG).

Table II. Absorption Maxima (kK) of [Mn(por)ClH$_2$O] in Pyridine

Band	Porphyrin						
	Etio	DMMepor	DMDepor	DMHpor	DMPrpor	TPP	Me pheo a
I	12.5[a]	12.5	$\sim$12.6	$\sim$12.5	12.4	12.0	$\sim$9.6
	$\sim$12.8	$\sim$12.8	12.9	12.9	$\sim$12.7	12.8	10.0
II	$\sim$14.3	$\sim$14.3	$\sim$14.3	$\sim$14.3	$\sim$14.2	$\sim$14.0	$\sim$11.6
	14.7[a]	14.7	14.7	14.6	14.6	$\sim$14.6	
III	$\sim$17.2	$\sim$17.2	$\sim$17.2	$\sim$17.2	$\sim$17.1	16.2	17.4
IV	18.2[a]	18.2	18.3	18.0	17.9	17.3	14.7
						19.0	
V	21.3[a]	21.2	21.4	21.2	21.0	21.0	21.3
V$_a$	$\sim$23.8	$\sim$23.8	$\sim$23.8	$\sim$23.8	$\sim$23.5	24.7	23.2
VI	27.1[b]	27.0	27.2	26.8	26.5	26.2	26.7
R(V/VI)	0.60	0.60	0.67	0.67	0.60	1.52	0.48

[a] ±0.1 kK. [b] ±0.2 kK.

bands, V and VI, in the 20–28-kK range. In general, band VI is more intense than band V by a factor of 1.5–2.0. The TPP complex is somewhat different, showing band V more intense than band VI. In fact, the near-uv bands are considerably weaker for this porphyrin than for other porphyrins. (See Figures 2 and 4 for a comparison.) Because of this, the usually weak absorption at $\sim$24 kK and the blue shoulder at $\sim$29 kK appear to be prominent features of the TPP spectrum. Although more difficult to pick out, these features can be seen for all other porphyrinmanganese complexes. The spectrum of the methyl pheophorbide a complex is typical of that of a chlorin and a manganese(III) complex. Band IV is intense while band III is relatively weak, as is the case for most metallochlorins. Bands V and VI are clearly present. The spectra of all the complexes in pyridine solution are again similar to each other. The general display resembles those for the chloroform solutions, except that bands III, IV, and V are blue-shifted while band VI is red-shifted in pyridine. Bands I and II can sometimes be resolved into two components (see Figure 2). The magnetic circular dichroism spectrum of a typical porphyrin complex, protoporphyrin IX dimethyl ester, was determined. The MCD spectrum and the corresponding absorption spectrum are shown in Figure 4. The frequency and sign of the prominent maxima in the MCD are 16.4 kK (−), 16.9 (+), 17.4 (−), 17.8 (+), 20.8 (−), 21.5 (+), 23.8 (+), 25.6 (+), 27.5 (−), 30.3 (+). The MCD spectrum shows overlap of A terms[12] for bands III and IV, an A term for band V, and a complex pattern of at least three features for band VI. Unfortunately, the region of bands I and II was not instrumentally accessible.

Discussion

The visible spectra of most metalloporphyrins are closely similar to each other, showing an intense B band at $\sim$24 kK and two weaker Q bands at $\sim$18 kK.[13] Replacing one metal for another only shifts the band position slightly. This was taken to indicate that the transition metal and porphyrin π levels are only weakly interacting.[3] The most spectacular exception to this general rule is the manganese(III) porphyrins. While the Q bands appear in the spectrum, the normally intense B band seems to be split into two less-intense bands. In addition, two weak bands appear in the near-ir. The anomalous visible spectrum of the Mn(III) complexes may be related to a significant metal–porphyrin π interaction.[1]

For Mn(III), with effective D_{4h} symmetry, the e_g (d_{xz}, d_{yz}) orbital is of proper energy and symmetry to interact with the e_g^* (π) orbital on the porphyrin. The metal→ligand π overlap would be greatest if the metal were in the plane of the porphyrin.[14] This geometry also leads to the strongest σ interaction between the metal and the four pyrrole nitrogen donors of the ligand. This is just another example of the well-known synergic bonding in metal complexes; *i e.*, charge build-up by strong σ donation from the ligand to metal is relieved by back π donations from the metal to ligand.[15] A qualitative energy level diagram, similar to that of Gouterman's Fe(III) scheme,[2] is given in Figure 5. Since all Mn(III) porphyrins have a high-spin d^4 configuration, only four d orbitals are singly occupied and the strongly antibonding b_{1g} orbital remains empty. An important point here is that, in contrast to the iron case, the stable high-spin configuration can be maintained for Mn(III) even when the metal is in the plane of the porphyrin.[16] The energy of the a_{1g} level is somewhat depressed since axial interaction should not be very great with the steric interaction of the axial ligand and the porphyrin π cloud. Further, the e_g ($d\pi$) metal level is depressed because it is bonding with respect to the back π bonding to the porphyrin. The relative position of the e_g and b_{2g} levels may very well be reversed.

A tentative assignment of the visible absorption bands of Mn(III) porphyrins can be made based on the above model. The lowest energy allowed charge-transfer bands are the porphyrin to metal a_{2u}, $a_{1u} \rightarrow e_g$ ($d\pi$) transitions. Just as the configuration interaction

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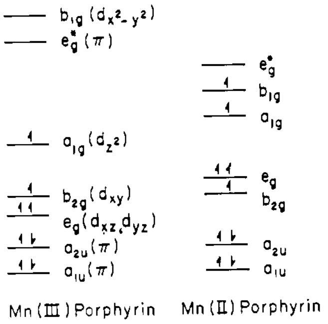

Figure 5. Qualitative molecular orbital diagram for porphyrin-manganese complexes.

of the $a_{1u} \rightarrow e_g^*$ and $a_{2u} \rightarrow e_g^*$ porphyrin states gives rise to the B and Q bands, a similar process should occur for the charge-transfer transitions. Bands I and II and band V can be assigned to a_{1u}, $a_{2u} \rightarrow e_g$ ($d\pi$) charge-transfer transitions. The assignment of band V to a charge-transfer transition has been previously suggested.[17] The apparent splitting of bands I and II in pyridine solution may be related to a slight splitting of the metal $d\pi$ level (d_{xz}, d_{yz}). A similar phenomenon has been observed for porphyriniron complexes in ferrimyoglobin.[18] In the latter case, Eaton and Hochstrasser have assigned the weak near-ir absorptions to a_{1u}, $a_{2u} \rightarrow d\pi$ charge-transfer absorptions on the basis of polarized absorption spectra measurements. In the same study the charge-transfer bands in the visible are assigned to a_{2u}' (π) and b_{2u} (π) $\rightarrow d\pi$ transitions. The ligand levels, a_{2u}' and b_{2u}, are the next highest filled π bonding levels just below the a_{1u}, a_{2u} levels. An intriguing possibility would be that band III in the porphyrin–Mn(III) spectrum is assigned to the same charge-transfer transition. It is tempting to assign this band to one of the Q bands normally seen in the metalloporphyrin spectrum. There are several reasons in favor of assigning band III to a charge-transfer band instead of to a $\pi \rightarrow \pi^*$ transition of the porphyrin ligand. The first of these is the observation that the separation of band III and band IV is 0.9 kK while that for vibrational components of the Q band is about 1.2 kK.[13] The second piece of evidence that indicates that band III and band IV originate in different electronic transitions is obtained from the MCD spectra. Both bands III and IV show sharp A terms of near equal magnitude. Conversely, the MCD spectra of divalent metalloporphyrins show only one strong A term and a much weaker (washed out) A term for the Q bands.[19] A reasonable assignment of bands III and IV would be that band III is due to a charge-transfer transition $b_{2u} \rightarrow d\pi$ and band IV is due to the ligand transitions a_{1u}, $a_{2u} \rightarrow e_g^*$. Reversing the assignments would also be qualitatively consistent with the data.

Band IV then can be related to a usual Q metalloporphyrin band. Likewise, the higher energy band, VI, can be related to the usual B band. The lower intensity and broadening can be ascribed to an admixture of charge-transfer character into these transitions.[20] The average energy of the Q and B bands of the corresponding metalloporphyrin[13] is lower than the average energy of bands IV and VI. This is in agreement with the notion that the π bonding in the manganese complex destabilizes the e_g^* (π) ligand orbital. The MCD spectrum is rather complex in the region of band VI showing a plus–minus–plus pattern of bands. The center component appears near the maximum of band VI. An analogous pattern of bands is seen for the MCD spectrum of high-spin iron(III) porphyrins in the B band region.[19] This pattern cannot be interpreted simply as the overlap of two A terms arising from the vibrational components of a vestigial B band. The latter case pertains for most divalent metalloporphyrins. The MCD spectrum near band VI may be complicated by the presence of charge transfer and other porphyrin terms. The fact that band V_a does not give rise to an A term strongly suggests that this band arises from a transition to nondegenerate level. This is consistent with another of the allowed porphyrin-to-metal transitions, $a_{,1u}$ $a_{2u} \rightarrow d_{z^2}$. The intensity of the charge-transfer bands in the absorption spectra is surprisingly high. This can be attributed to the substantial porphyrin π character of the e_g ($d\pi$) level. Conversely, the intensity of the $\pi \rightarrow \pi^*$ bands is lower than normal since the e_g^* level is no longer a pure porphyrin orbital.

The effect of axial ligand and solvent on the visible spectrum of Mn(III) porphyrins has been studied.[1,5] There is a general red shift of all the bands as the polarizability of the anion or solvent molecule increases. Stabilization of the excited state of the porphyrin π system by the axial anion, donor molecule, or solvent molecule is expected for molecules of this sort.[21] Axial ligation probably involves a steric interaction with the porphyrin π cloud and may not significantly involve σ or π interaction with the metal orbitals. With a variety of anion donors that display a wide variation in π donor and acceptor and σ donor properties, no selective band shifts are noted; *i.e.*, all bands are shifted in the same direction.

A nonspecific band shift of similar magnitude is also seen when the in-plane macrocycle is varied. Disregarding TPP for the moment, the variation of maxima with porphyrin is not large, ranging from 0.1 kK for band II to 0.8 kK for band VI. There appears to be a wide gap between TPP and the other porphyrins. Within experimental uncertainty, all of the absorption maxima are shifted in the same way by variations in the substituents of the porphyrin. For example, the energy order of band VI is DMDepor > Etio > DMMesopor > DMHpor > DMPrpor > TPP. Except for the first member of this series, the other porphyrins fall in the order of their pK_a values.[22] The stronger the porphyrin σ donor, the higher the energy of the transitions. The same trend is observed for the corresponding planar nickel porphyrins.[22] Electron-donating substituents place negative charge into the macrocycle and the porphyrin bonding and antibonding π levels move further apart.[23]

There is only a slight variation in band intensity

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among the first five porphyrins. On the other hand, the tetraphenylporphin derivative shows weak near-ir bands and the weakest absorption in the 27.0-kK region of all the porphyrins studied. Either the β hydrogen substituents or the *meso* substituents may account for the relatively weak tetraphenylporphin spectra. The intensity behavior for TPP complexes in general appears to be opposite that of fully β-substituted porphyrins. For example, the oscillator strength of the Q band is found to increase with the extent of metal interaction for octaalkylporphyrins while it is found to decrease for the tetraphenylporphins.[22] It has recently been noted that while the a_{2u} is at higher energy than the a_{1u} level for most metalloporphyrins, the reverse is true for tetraphenylporphin metal complexes.[24] This fact might be related to the intensity difference noted here. The intensities of bands V and VI for different anion derivatives[1,5] vary with respect to each other; *i.e.*, as the intensity of V increases, that of VI decreases. This intensity borrowing may be related to an increase in metalloporphyrin π mixing. The intensity ratio of band VI to band V for the porphyrins, in both chloroform and pyridine, is TPP > DMDepor > DMHpor > DMPrpor > DMMesopor > Etio. This could imply a decrease in manganese–porphyrin π mixing in going to the right of the order. What is more likely is that it reflects subtle changes in the electronic transitions upon β substitutions that are more or less independent of the manganese–porphyrin interaction.[23]

(Methyl pheophorbide a)manganese(III) spectra represent a variation of the porphyrin case. In the chlorin two of the β ring positions of the porphyrin are reduced and, as a result, the highest filled and lowest empty π MO of the porphyrin are altered. The filled a_{2u}, a_{1u} levels of the porphyrin are no longer accidentally degenerate, with the a_{2u} level remaining at the same energy while the a_{1u} level is raised in energy.[25] Conversely, the doubly degenerate empty e_g^* level is split for the chlorins, giving one level of slightly higher energy and another at still higher energy. Transitions among the four orbitals give rise to a strong Q_y band at low energy, a weak Q_x band at an energy comparable to the porphyrin case, and two closely spaced B bands at higher energy, again comparable to that of porphyrins. For the Mn(III) chlorophyll derivative the near-ir bands are substantially less intense and red-shifted by ~2.5 kK from the porphyrins. On the other hand, the positions of bands III, V, and VI are practically the same as for the porphyrin complex, while band IV is considerably red-shifted. This supports the view that this band can be assigned to the Q_y band. Similarly, band VI can be assigned to the B band. The absorption is broadened and blue-shifted from the B band for divalent metallochlorins.[26] This is in agreement with the notion that manganese-to-porphyrin π mixing is present in these complexes.

Like the porphyrin case, a reasonable assignment of bands I, II, and V would be to the porphyrin-to-metal charge-transfer transition $a_{1u}, a_{2u} \rightarrow e_g^*$. The fact that bands I and II are shifted to considerably lower energy in going from the porphyrins to the chlorins would agree with the notion that the highest filled π MO, a_{1u}, has been destabilized in the chlorins. As for the porphyrin complexes, band III can be assigned to a porphyrin-to-metal charge transfer $b_{2u} \rightarrow d\pi$. The relatively low intensity of the charge-transfer bands may be a consequence of the lowering of the porphyrin π character of the $d\pi$ metal orbital. The destabilization of the split e_g levels in the chlorin would decrease the metal→porphyrin π mixing. Another factor in this may be the molecular structure of the chlorin macrocycle. A nonplanar structure would lead to less efficient σ donation and π acceptor ability of the chlorin ligand. In general, the position of the bands for the methyl pheophorbide a complex places the macrocycle at the lower end of the energy order given above. This agrees with the observed lower donor ability (lower pK_a) of chlorins than for porphyrins.[11]

Mn(III) porphyrins can be reduced to Mn(II) porphyrins with some difficulty. The stability of Mn(III) porphyrins is surprising, *e.g.*, $E°$ for Mn(III) → Mn(II) is ~ -0.3 V.[27] The strong σ and π interactions of manganese(III) and the porphyrin would account for this stability. The Mn(II) complexes have a high-spin d^5 configuration[6] with the fifth electron occupying the $d_{x^2-y^2}$ orbital. The energy of the $d_{x^2-y^2}$ level must be low. This implies that the Mn(II) will be out of the plane of the porphyrin as is the case for the analogous high-spin Fe(III) porphyrins.[16] This geometry does not favor metal→porphyrin π bonding and, as a consequence, the visible spectrum of Mn(II) porphyrins is normal.[6] Polarographic measurements show axial ligation is stronger for Mn(II) than for Mn(III).[28] This is consistent with the notion that the metal is accessible to the ligand and is not buried in a sterically interacting π cloud, as is the case for Mn(III).

High-spin porphyriniron(III) complexes also show characteristic weak near-ir absorption bands.[2] As discussed above, these have been assigned to porphyrin π to iron d orbital transitions $a_{1u}, a_{2u} \rightarrow d\pi$.[2,17] The position of the maximum is very sensitive to the axial ligand with a spread of nearly 2.0 kK in going from the methoxide ligand to the iodide.[29] The ligand order corresponds approximately to the one found for manganese(III) porphyrins.[5] However, the corresponding spread for manganese(III) is only 0.5 kK. The increased sensitivity of the axial interaction for iron(III), in comparison to manganese(III), can be related to the molecular structure of high-spin iron(III) porphyrins. If the several examples that have been determined by X-ray methods are typical of this sort of complex, then the iron atom should be about 0.5 Å out of the plane of the porphyrin for high-spin iron(III) porphyrins.[16] In this position the iron atom can bind in a fairly specific way to the axial anion since the steric interaction with the porphyrin π cloud will not be great. The charge-transfer bands of the high-spin Fe(III) porphyrin appear to be red-shifted from those of the Mn(III) porphyrins. This is consistent with the increasing stability of the metal d orbitals in going from

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manganese to iron. The iron(III) porphyrins do not show an intense charge-transfer band in the 20.0–25.0-kK region as do the manganese(III) porphyrins. Of course, weak charge-transfer bands in this region may be buried under more intense porphyrin transitions. In fact, the broadened α,β bands may indicate several unresolved absorption maxima in this region. In support of this, MCD spectra do reveal additional features in this region.[19] The intense nature of the charge-transfer bands for Mn(III) can be related to strong $d\pi$–$e_g{}^*$ mixing in these complexes. The absence of this band for Fe(III) porphyrins may be taken as evidence for a much weaker interaction in these materials. The fact that a normal B band is observed for Fe(III) porphyrins (in contrast to the Mn(III) case) also suggests this.[2] On the other hand there is ample evidence that some π bonding does occur in Fe(III) porphyrins.[27] The difference in behavior between Fe(III) and Mn(III) porphyrins may be due to the stability of the metal d orbitals or to a difference in molecular structure. The increased stability of the iron d orbitals increases the energy mismatch of the $d\pi$ orbitals and $e_g{}^*$ porphyrin orbitals and could lower the π interaction. Further, the square-pyramidal structure for the Fe(III) porphyrins places the iron atom in a less favorable position for metal–porphyrin π overlap.

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