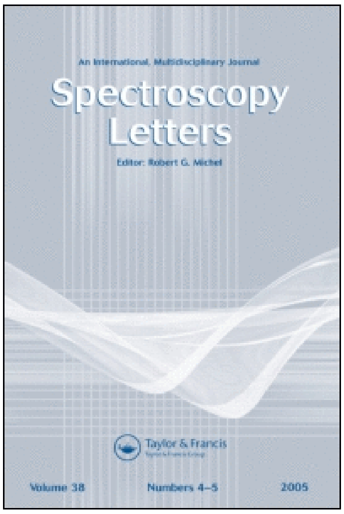

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Magnetic Circular Dichroism Studies of the Low-Energy Absorption Bands of Mn(III) Porphyrin Complexes

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MAGNETIC CIRCULAR DICHROISM STUDIES OF THE LOW-ENERGY ABSORPTION BANDS OF Mn(III) PORPHYRIN COMPLEXES

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INTRODUCTION

Porphyrin manganese complexes are of interest, both from their possible involvement in oxygen formation in photosynthesis and as analogues to the biologically important iron porphyrin complexes. Recent studies by Boucher$^{(1-3)}$ have indicated that porphyrin manganese III complexes exhibit a unique absorption spectrum indicative of an unusual electronic structure. Their spectra are considerably more complex than other metalloporphyrins, e.g., heme proteins, which typically exhibit visible absorption spectra containing two prominent bands (α,β) in the 16 to 20-kK region and a third, more intense band, the Soret band, at 23 to 25 kK.

The Soret and α bands are $\pi^* \leftarrow \pi$ transitions arising from the $e_g^* \leftarrow a_{1u}, a_{2u}$ excitations, while the β band is, from MCD evidence, charge transfer in nature.$^{(4)}$ The spectra of manganese III porphyrins consist of at least six bands which have been labeled by Boucher as I through VI. For convenience, we shall retain his nomenclature throughout this paper. These spectral differences are not obviously related to the +3 charge of the metal since other three-valent metal porphyrin complexes, e.g., those of Co and Fe, give rise to normal porphyrin spectra. A recent study by Eaton and Charney$^{(5)}$ identifies the infrared bands at 10 to 16 kK in ferrocytochrome C as d-d bands by circular dichroism measurements.

For species that give rise to normal spectra, it is generally accepted that the metal and the porphyrin π systems are only weakly interacting. In view of the abnormal spectroscopic behavior of the Mn(III) porphyrin systems, the weakly interacting model is evidently invalid. It is thus of importance that their spectra be understood as an aid to our general understanding of metalloporphyrin structure and as an aid to a possible unequivocal establishment of the presence or absence of such species in chloroplast preparations.$^{(2)}$

EXPERIMENTAL

The optical spectra were obtained on a Cary 14 spectrophotometer, using a 1-mm path length cell. The MCD spectra were obtained from a locally constructed spectrometer especially designed for work in the far red (to 1.05 microns) spectral region. It has been described elsewhere.(6) The short path length (1 mm) was required because of the electromagnet (Varian 4-in. with bored tapered pole pieces).

The MCD spectra were not calibrated on an absolute basis, but were compared with a standard, magnesium phthalocyanine, under identical conditions. As such, the absolute accuracy of the $[\theta]_{sp}$ scales is about ±20%, but the relative accuracy between spectra is much greater than that. This procedure is less than ideal, but was necessary because the absolute calibration via ORD or MORD is not possible, and because very few CD spectra have been measured in this spectral region. (The peak-to-peak $[\theta]_{sp}$ for magnesium phthalocyanine $Q_{0\text{-}1}$ band was taken to be $110 \cdot 10^{-4}$,(5) and the magnetic field was $2.2 \cdot 10^{4}$ gauss.)

The error due to finite slit width in the MCD spectra of the Mn porphyrins was calculated to be less than 1%.(7)

The porphyrin samples were supplied by Dr. L. J. Boucher of Carnegie Mellon University.

RESULTS

Optical and MCD spectra of bands VI through III of a series of Mn(III) porphyrins have already been discussed by Boucher.(3) In this paper, experimentally, we shall concern ourselves solely with the low-energy MCD spectra, i.e., Bands I and II. In our discussion of spectral assignments, where necessary, reference will be made to the MCD spectra of reference 3.

The low-energy optical and MCD spectra of a chloroform solution of aquo (iodo) manganese III protoporphyrin IX dimethyl ester (DMPrPorIH_2O) are illustrated in Figures 1-a and 1-b, respectively, while the corresponding spectra of the same compound in pyridine solution, i.e., [DMPrPor$(pyr)_2$], are illustrated in Figures 2-a, 2-b, and 2-c. In the nomenclature of Boucher, the optical spectrum in each case appears to consist of the two absorption bands, i.e., Bands I and II. Their MCD spectra differ significantly as may be seen from a comparison of Figures 1-b, 2-b, and 2-c. In chloroform solution, Band I gives rise to an A term with a strong B interaction, and Band II gives rise to a B term of opposite sign to the B term of Band I. In pyridine solution, however, Band I gives rise to a complex MCD pattern that may be due to a B term overlapping the A term from Band I. Band II gives rise to a B term of the same sign as that observed from DMPrPorIH_2O in chloroform solution. The A term from Band III apparently shifts the B maximum from the absorption maximum.

Low-energy optical and MCD spectra of aquo (chloro) manganese III etio porphyrin in chloroform [Etio (ClH_2O)] and pyridine [Etio $(pyr)_2$] are illustrated in Figures 3 and 4. Both the optical and MCD spectra of the chloroform solution are very similar to those obtained from

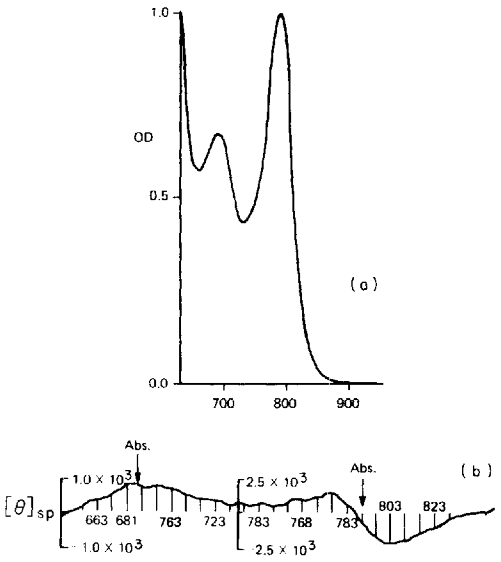

FIG. 1

Low-Energy Optical and MCD Spectra of Aquo (Iodo) Manganese III Protoporphyrin IX Dimethyl Ester in CHCl$_3$ Solution.

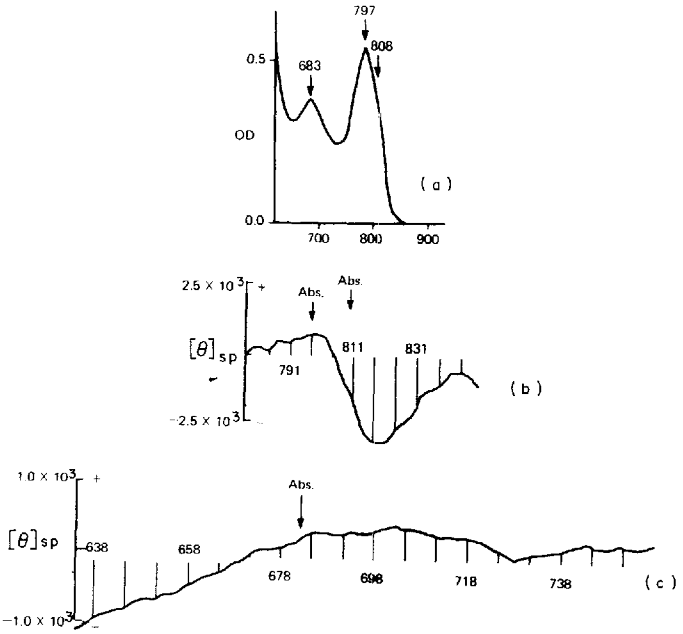

FIG. 2

Low-Energy Optical and MCD Spectra of Manganese III Protoporphyrin IX Dimethyl Ester in Pyridine Solution.

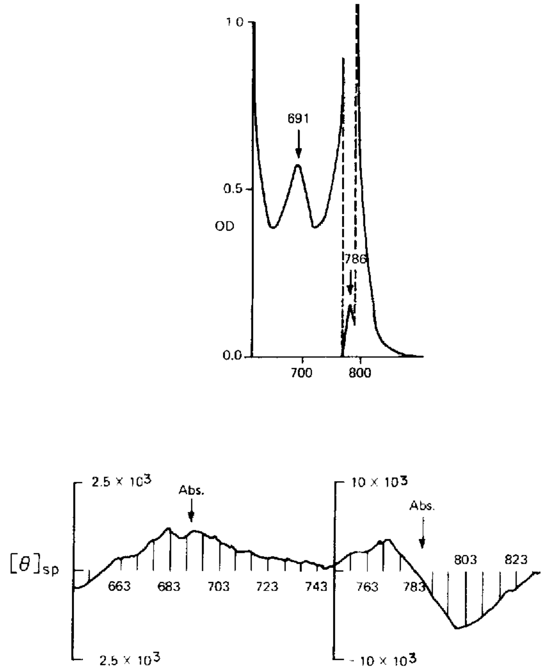

FIG. 3

Low-Energy Optical and MCD Spectra of Aquo (Chloro) Manganese III Etio Porphyrin in $CHCl_3$ Solution.

the chloroform solution of DMPrPor(H_2O). Here again, the MCD spectrum of Band I is consistent with a combination of an A term with strong B interaction and Band II gives rise to a B term of opposite sign to the B term of Band I. In pyridine solution, however, both the optical and MCD spectra are different to those obtained in chloroform solution. Noticeable in the optical spectrum is the splitting of Band II into two components. In the MCD spectrum, it can be seen that the two components of Band II give rise to two B terms of opposite sign, the lower energy band having a B term of the same sign as Band II in DMPrPor.

The peak positions, optical densities, and MCD amplitudes for all four spectra are tabulated in Table 1.

DISCUSSION

It can be seen from the results just presented that the low-energy spectrum, which has been referred to as Bands I and II, in two cases consists of at least three absorption bands. Thus, with the four and sometimes five bands that occur to higher energy, it is necessary for Mn(III) porphyrin complexes to account for at least seven and possibly eight absorption bands which fall in the visible and near infrared.

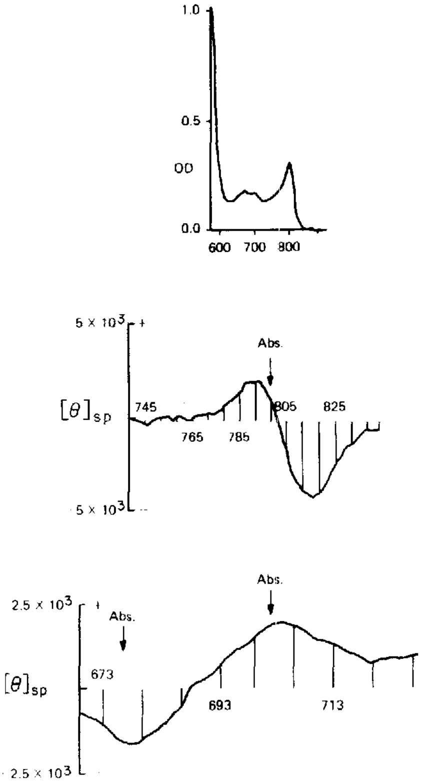

FIG. 4

Low-Energy Optical and MCD Spectra of Manganese III Etio Porphyrin in Pyridine Solution.

TABLE 1

Absorption and MCD Parameters

			Band I								Band II		
Species	lc $\left(\frac{mg\ cm}{ml}\right)$	O.D.	MCD Type and Amplitude × 10^{-3}	λ_0 (nm)	$\Delta\lambda$ (nm)	O.D.	MCD Type and Amplitude × 10^{-3}	λ_0 (nm)	$\Delta\lambda$ (nm)	O.D.	MCD Type and Amplitude × 10^{-3}	λ_0 (nm)	$\Delta\lambda$ (nm)
Mn(III) DM PrPor(IH$_2$O)	5.2	1.01	A 3.6 B 1.3	780	43					0.18	+B 0.26	690	32
Mn(III) DM PrPor(pyr)$_2$	2.45	sh	A 3.9 –B 1.3	808	32 (from MCD)	0.53	See Spectrum B	797	48	0.11	+B 0.52	683	41
Mn(III) Etio (ClH$_2$O)	4.1	1.15	A 12.5 –B 3.7	786	42					0.19	+B 1.0	691	31
Mn(III) Etio (pyr)$_2$	1.1	0.31	A 6.2 B 1.7	798	29	0.04	B 1.6	677	36	0.04	+B 1.5	703	23

In all cases, the qualitative features may be rationalized on the basis of a model suggested by Boucher with some modifications. As this author has previously suggested, for Mn(III) porphyrins with effective D_{4h} symmetry, the e_g (d_{xz},d_{yz}) orbital is of proper energy and symmetry to interact with the $e_g^*(\pi)$ orbital on the porphyrin, with the metal-ligand π overlap being greatest if the metal were in the plane of the porphyrin. In this configuration, the axial interaction should be weak, and hence the $a_{1g}(d_{z^2})$ level will be depressed and has been taken, in our orbital scheme, to be weakly antibonding with Cl^- and I^- ligands (Case I). With pyridine ligands (Case II), it is more strongly antibonding. The $b_{1g}(d_{x^2-y^2})$ orbital is taken to be strongly antibonding, while the $b_{2g}(d_{xy})$ is assumed to be slightly antibonding. An approximate molecular orbital diagram is illustrated in Figure 5.

In Case II, with the pyridine ligands tending toward an octahedral complex, the $a_{1g}(u)$ orbital increases in energy, and may cross the e_g level. The e_g orbital is placed on the left of the diagram along with the porphyrin π orbitals. For weakly interacting metal-porphyrin complexes, this orbital is predominantly metal in character. However, in the model we have chosen, it is assumed that the interaction is sufficiently strong for this orbital to have largely lost its identity as a metal orbital. Both it and the e_g^* orbital must be considered as admixtures of metal (d_{xz},d_{yz}) and porphyrin (π) orbitals. In this scheme, the $\pi^* \leftarrow \pi$ electronic spectrum is considered to arise from excitations between the six π orbitals labeled m,n,p,q,r, s with the ground state distribution being as shown in the figure.

Excitations p,q ← n and p,q ← m give rise to a total of four states which occur as two doubly degenerate pairs. Depending upon the extent of the delocalization of the metal e_g orbitals into the porphyrin π system, two situations arise with respect to the excitations r,s ← n and r,s ← m. If the delocalization is low, i.e., the porphyrin and metal π orbitals are not strongly coupled, then excitations r,s ← m and r,s ← n also give rise to a total of four states which occur as two doubly

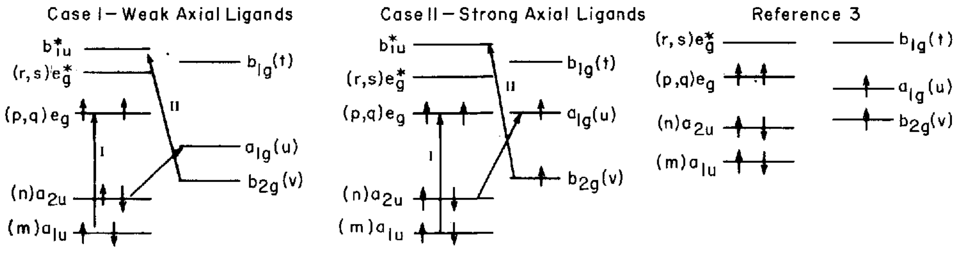

FIG. 5

Qualitative Molecular Orbital Diagram for Porphyrin Manganese III Complexes degenerate pairs. However, if the porphyrin metal π mixing is extensive, then the same two excitations each give rise to three doubly degenerate excited state configurations. Of this total of six degenerate excited state configurations, four are electric dipole allowed and hence have appreciable intensity, while the other two will have zero predicted intensity. The four allowed states will give rise to two pairs of absorption bands. Without a prior knowledge of the molecular orbital coefficients, it is not possible to predict the splitting that will occur between each pair. The separation will, however, be relatively small and equal to the term

$$\Delta = 1/2 < nq | qn > + 1/2 < nr | rn > - 1/2 pq | qp > - 1/2 < pr | rp > + < np | pn > + < qr | rq >$$

where

$$< pr | rp > = \int \phi_p(1)\, \phi_r(2)\, (e^2/r_{12})\, \phi_r(1) \phi_p(2)\, d\tau$$

Thus, on the first basis, we will expect four absorption bands from the four excitations, whereas on the second basis we can expect six absorption bands. In each case, the states giving rise to the absorption bands will have E_u symmetry, and, hence, contribute an A term in the MCD spectrum. Since configuration interactions between all states arising from these four excitations have also to be considered, a detailed knowledge of the wave functions is necessary before any reliable prediction of either the energies of relative intensities of the various bands can be made. However, from a total of four excitations, we can expect a minimum of six absorption bands, each of which will have E_u symmetry, and, hence, contain an A term in the MCD spectrum.

Two further transitions which are considered to contribute to the observed spectrum are the transitions u ← n and b_{1u} ← v. These transitions are both electric dipole allowed, give rise to nondegenerate excited states and, on the basis of the orbital scheme, would have approximately equal energy. However, since these two excitations do not have an orbital in common, they undergo no magnetic dipole interaction, and, hence, will not contribute a B term to each other in the MCD spectrum.

Based upon this model, the electronic absorption band that gives rise to the A term in Band I may, in all cases, be identified as the lower energy component of the two doubly degenerate states that arise from the p,q ← n, m excitations. In order to assign the Band II system, let us first compare the low-energy optical and MCD spectra of Etio (ClH_2O) in chloroform and pyridine (Figures 3 and 4). In pyridine solutions, the band is found to split into two components which give rise to two B terms of opposite sign. In chloroform solution, on the other hand, a single peak is observed which exhibits a B term of the same sign as the lower energy component of the split band system observed in pyridine solution.

The MCD spectrum of Etio $(pyr)_2$ indicates that Band I consists of an A term with weak B interaction. The optical spectrum, however, gives some evidence for the presence of a shoulder on the high-energy side, which appears to make no contribution to the MCD spectrum. With the molecular orbital scheme of Figure 5, these results are consistent with the following assignments. For the pyridine complex, Band II consists of the two excitations $b_{1u} \leftarrow v$ (703 nm) and $u \leftarrow n$ (677 nm). These two transitions have no orbital in common, and, hence, would not interact strongly with each other.

The transitions $u \leftarrow n$ will also magnetically mix with the transition $p,q \leftarrow m,n$ to give rise to a B term in the MCD spectrum. The shoulder on the high-energy side of Band I which makes no contribution to the MCD spectrum can be tentatively assigned to the d-d band arising from the transitions $t \leftarrow v$. This transition has no orbital in common with any other excitation, and, hence, would be expected to make little or no contribution to the MCD spectrum.

In the chloroform complex [Etio (ClH_2O)], Band II is a single band which gives rise to a single B term in the MCD spectrum, whereas Band I is now complex, consisting of at least two transitions. Here, we believe that Band II may be identified with the transition $b_{1u}^* \leftarrow v$ as before, while the transition $u \leftarrow n$, which contributed to the Band II system of the pyridine solution, has now moved to much lower energy and is not observed.

In the corresponding DMPrPor complexes, Band I is identified by the A term. In DMPrPor (IH_2O), Band II is $b_{1u}^* \leftarrow v$ and $u \leftarrow n$ is not observed. In DMPrPor $(pyr)_2$, the distortion of the A term of Band I appears to be due to $u \leftarrow n$, while Band II is normal ($b_{1u}^* \leftarrow v$).

The MCD spectra of Bands III, IV, V, and VI of DMPrPorClH_2O in chloroform solution, have been discussed by Boucher(3). Bands III and IV give rise to an overlap of A terms, Band V an A term, and Band VI a complex pattern containing at least three features. A further feature in the MCD spectrum is an A term which coincides with a very weak absorption band at ca 24 kK.

Our assignments of these transitions largely agree with those of Boucher, the principal differences being the assignment of Bands III and Va. With the second model we present, both Bands III and IV are considered to arise from the transitions $r,s \leftarrow m, n$, whereas on the first model the assignments reduce to that of Boucher in that one or the other of the transitions has to arise from a lower energy porphyrin π orbital and consists of excitations of an electron from this level to the "metal" $e_g(p,q)$ level. Although there is no definitive way of distinguishing between the two possibilities with the available information, we feel that the second model has some merit, when we consider Band VI. From the work of Boucher, this band gives rise to a complex pattern containing at least three features. On the basis of the second model, the complex magnetic circular dichroism behavior can be taken to arise from the interaction between the higher energy pair of bands arising from the $e_g^* \leftarrow a_{1u},a_{2u}$ ($r,s \leftarrow m, n$) transitions with a second transition of equal energy. This avoids the necessity of requiring the accidental

TABLE 2

	Model I	Model II	Reference 3
I	$p, q \leftarrow n, m$ $t \leftarrow v$	$p, q \leftarrow n, m$ $t \leftarrow v$	$p, q \leftarrow n, m$
II	$b^*_{1u} \leftarrow v$ $u \leftarrow n$	$b^*_{1u} \leftarrow v$ $u \leftarrow n$	$p, q \leftarrow n, m$
III	$p, q \leftarrow b_{2u}$	$r, s \leftarrow n, m$	$p, q \leftarrow b_{2u}$
IV	$r, s \leftarrow n, m$	$r, s \leftarrow n, m$	$r, s \leftarrow n, m$
V	$p, q \leftarrow n, m$	$p, q \leftarrow n, m$	$p, q \leftarrow n, m$
Va	$u \leftarrow ?$	$u \leftarrow ?$	$u \leftarrow n, m$
VI	$r, s \leftarrow n, m$ $p, q \leftarrow b_{2u}?$ $u \leftarrow ?$	$r, s \leftarrow n, m$ $r, s \leftarrow n, m$ $u \leftarrow ?$	$r, s \leftarrow n, m$

near degeneracy of three bands arising from three different transitions which is required by the first model. A comparison of the assignments based upon both models and those of Boucher is illustrated in Table 2.

Band Va has been taken by Boucher to arise from the transitions $u \leftarrow n, m$. Since we have found it necessary to assign the transitions $u \leftarrow n$ to the Bands I and II system, Band Va could arise from a transition from some lower energy nondegenerate porphyrin π orbital into the d_{z^2} level.

The main differences between the assignments made in this present work and those presented by Boucher arise from the requirement of four excitations to fit the complex MCD behavior of the Bands I and II system. With the recognition that the considerable mixing of the metal π orbitals with the porphyrin II orbitals takes place, both the high intensity of the "charge transfer" states and the low intensity of what are normally considered $\pi^* \leftarrow \pi$ states can be readily understood. Furthermore, since in the ground state the manganese $d\pi$ (e_g) electrons are delocalized onto the porphyrin ring, this could facilitate the oxidation of the manganese III to the manganese IV state by molecular complex formation. This may be an important factor in a system such as a chloroplast, if indeed the role of manganese in such a system is that of a redox enzyme.

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