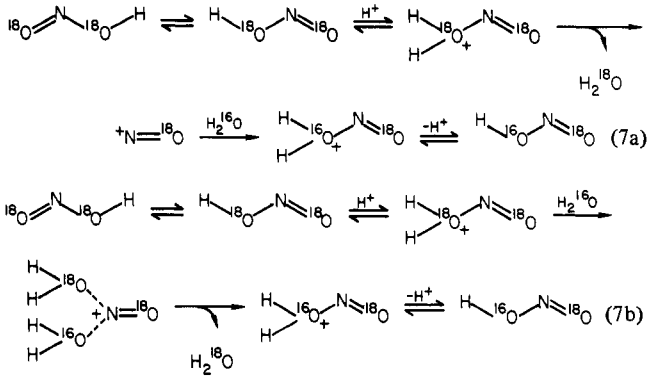

We have demonstrated that ^{18}O does exert an isotope effect on the ^{15}N NMR signal of the ^{15}N-enriched, ^{18}O-labeled nitrite ion. The magnitude of the isotope-induced shift was 0.138 ppm/^{18}O, and the isotope shift was additive. We have also shown that the ^{18}O-isotope effect in ^{15}N NMR can be applied to the field of physical-inorganic chemistry. Nitrogen(oxygen)-water exchange reactions can be followed in greater detail than has been possible previously since ^{15}N NMR permits a direct quantitation of the different ^{18}O-isotopically labeled nitrogen species. This new technique was used to examine an acid-catalyzed medium nitrite(oxygen)-water exchange reaction in a continuous assay mode. The exchange was found to proceed by the sequential exchange mode as had been previously postulated from indirect evidence on the basis of the total ^{18}O content of the nitrite ion. We believe that the ability to directly quantitate the different isotopically labeled nitrogen species will provide an opportunity to study nitrogen(oxygen)-water exchange reactions in detail which heretofore has not been possible. In addition to mechanistic organic and physical-inorganic studies, applications may also be anticipated in many biological areas.

Acknowledgment. This investigation was supported by USPHS Research Grant GM 22933-04 from the National Institute of General Medical Sciences and by N.I.H. Grant RR 01077 from the Division of Research Resources. We thank Dr. Robert Santini for his instrumental design work which enabled us to obtain ^{15}N NMR spectra by using the NTC-470 spectrometer and Dr. John Kozlowski for his help in obtaining ^{15}N NMR spectra by using a Varian FT-80A spectrometer.

Use of Magnetic Circular Dichroism to Determine Axial Ligation for Some Sterically Encumbered Iron(II) Porphyrin Complexes

James P. Collman,*[1a] Fred Basolo,[1b] Edward Bunnenberg,[1a] Terrence J. Collins,[1a] John H. Dawson,[1c] Paul E. Ellis, Jr.,[1b] Matthew L. Marrocco,[1a] Albert Moscowitz,[1d] Jonathan L. Sessler,[1a] and Thomas Szymanski[1b]

Contribution from the Departments of Chemistry, Stanford University, Stanford, California 94305, Northwestern University, Evanston, Illinois 60201, the University of South Carolina, Columbia, South Carolina 29208, and the University of Minnesota, Minneapolis, Minnesota 55455. *Received February 27, 1981*

Abstract: The application of magnetic circular dichroism (MCD) as a fingerprint method for determining the spin state and axial coordination environment of a number of synthetic ferrous porphyrin complexes has been examined. The appearance of the MCD spectrum is a function of the spin state and the nature of the axial ligand or ligands. When these variables remain constant, the band shapes in the Soret region, but not the intensities, do not differ significantly within the series of porphyrins investigated here. For any given axial ligand or ligands, provided that spectra have been measured for a known example of each possible spin state and coordination environment to serve as standards, the shape of the MCD Soret band can be used as a qualitative marker of these key parameters. This determination is made on the basis of a single spectrum, and the advantages over other methods derive from the unique simplicity of the measurement. The coordination chemistry at iron(II) in the family of capped, pocket, and cofacial porphyrins studied here, as followed by MCD, can be used to determine, in a semiquantitative manner, the effects of the steric control of coordination features specifically incorporated into these porphyrin molecules. The design features and the steric effects are discussed. The MCD spectra are presented in graphic and tabular form, and the advantages and limitations of MCD as employed here are considered. The preparation and characterization of a mixed-metal, free-base, cofacial porphyrin is presented.

Introduction

Nature has chosen iron porphyrins to function at the active site in a number of biological systems that are indispensable to most forms of animal life.[2] These complex systems continue to inspire porphyrin-related research. Some quantity of the mechanics and properties of these systems can be ascribed to the various discernible features of metallochemistry, such as oxidation state, redox processes, type of ligation, ligand affinity, coordination number, and spin state. These properties are often influenced or controlled by interactions between the heme and the protein component. In order to learn more about heme-protein interactions associated with the activation, transfer, and storage of dioxygen, we, and others, have constructed synthetic analogues of the oxygen-binding centers in hemoproteins. These previously reported studies[3] have provided some assistance to our understanding of hemoproteins and have suggested new avenues of research.

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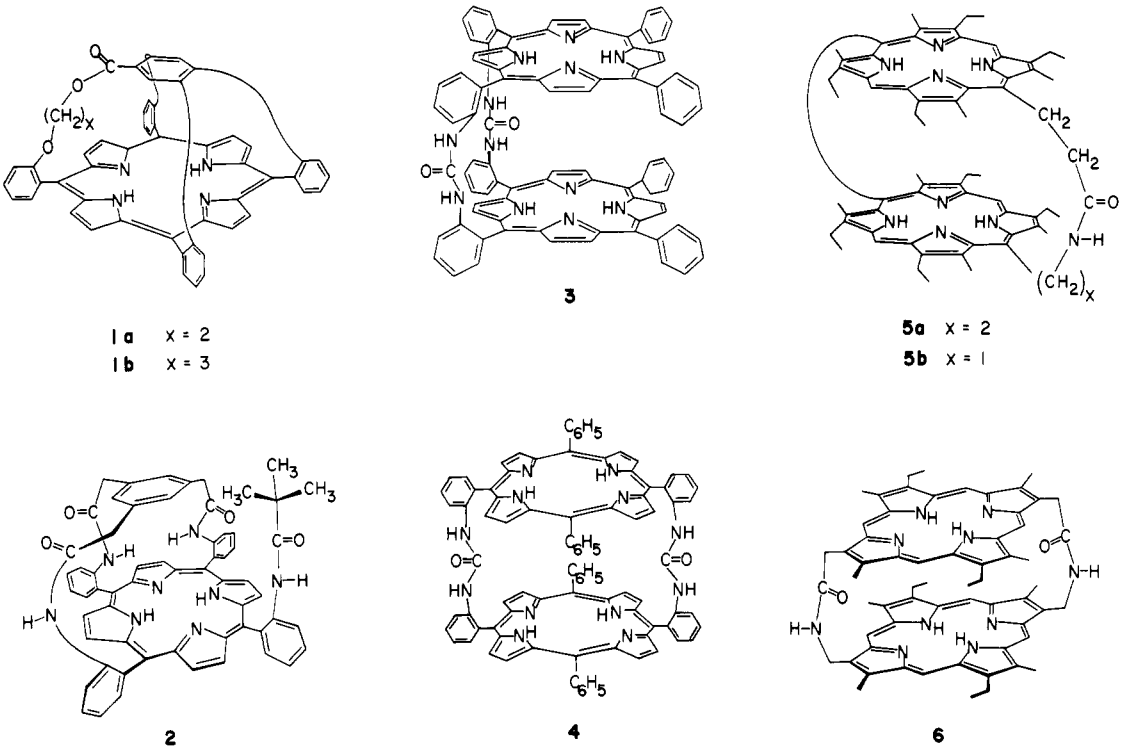

Figure 1. "Capped", "pocket", and "face-to-face" free-base porphyrins: H_2Cap, **1a**; H_2HmCap, **1b**; H_2PocPivP, **2**; H_4ClamDU, **3**; H_4FTFDU, **4**; H_4*m*-FTF6-3,2-NH, **5a**; H_4*m*-FTF5-3,1-NH, **5b**; $H_4\beta$-FTF4-2,1-NH, **6**.

In order to mimic the behavior of heme-containing biomolecules with oxygen and carbon monoxide, model systems must reproduce the control of coordination exhibited by the natural systems. Examination by model building of the role of steric effects on the distal side of the hemoprotein heme cavity in tuning the relative affinity of the heme for carbon monoxide and oxygen[4] is an exercise in developing control of coordination. Multielectron redox catalysts based on "face-to-face" porphyrins for the four-electron reduction of molecular oxygen to water have also recently been designed.[5] The control of coordination features that are part of the design of these molecular catalysts is apparently very important. It appears that oxygen must be able to interact simultaneously with the two metal centers in the molecule for effective catalysis to occur.

Studies of structure–function relationships of this nature would be greatly assisted by the existence of a method for defining the coordination at the metal in porphyrin complexes where more than one type of coordination state is possible. A number of spectroscopic and physical techniques, such as X-ray, magnetic susceptibility (either direct or from NMR), NMR, IR, resonance Raman, Mössbauer, and absorption spectroscopy, are available for this purpose. Each of these methods has certain limitations in the range, ease of application, or accuracy of the determination. We have found, however, that once standard spectra for all of the various possible coordination environments for each ligand type have been obtained, magnetic circular dichroism (MCD) provides a simple and unambiguous means of making spin-state determinations in solution for a broad range of synthetic iron(II) porphyrins. Because of the close connection between spin state and coordination number in most of these systems, MCD also affords a very useful simple probe of coordination environment.

In contrast to absorption spectra where bands are necessarily of one sign, MCD bands may be either of positive or negative sign, and adjacent bands are frequently of opposite sign. In addition, the particular kind of band (A-, B-, or C-term bands) observed is an intimate function of the electronic structure of the molecule.[6] For iron porphyrins, these factors combine to make MCD very sensitive to changes in oxidation state, spin state, and the nature of the axial ligands. MCD has been widely used in porphyrin[7] and heme protein[8,9] studies. Our own work has included studies on inositol hexaphosphate (IHP) induced spin-state changes in methemoglobin,[10] on cytochrome P-450,[11] and on a model compound for it.[12] In a recent publication[13] we introduced the application of MCD as a "fingerprint" technique for the spin state of synthetic iron(II) porphyrins, primarily in the context of tailed picket-fence porphyrins and their dioxygen complexes. Here we expand on this application and further illustrate the use of MCD as a technique for defining the coordination environment at the metal in ferrous porphyrin molecules, including some that have been designed to achieve specific features of coordination control (Figure 1). The existence of standard MCD spectra of ferrous porphyrin complexes of known coordination and spin state, under the experimental conditions used for (a) each axial base ligand or combination of ligands and (b) each possible coordination geometry for a given ligand, is clearly demonstrated to be a prerequisite to the application of MCD in the manner employed here.[14]

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Experimental Section

The following compounds were prepared as described in the literature:[16] H_2TPP,[2b] $H_2TPivPP$,[17] $H_2Piv_3(4CIm)P$,[13] H_2ADE,[5d] $H_4ClamDU$ (**3**),[5c] H_4FTFDU (**4**),[5c] H_4m-FTF6-3,2-NH (**5a**),[5d] H_4m-FTF5-3,1-NH (**5b**),[5d] $H_4\beta$-FTF4-2,1-NH (**6**),[5b] $H_2PocPivP$ (**2**),[18] H_2Cap (**1a**),[3b] and H_2HmCap (**1b**).[3b] Sperm whale myoglobin (grade A) was obtained from Sigma.

Ni(ADE). 5,15-Bis(carbethoxymethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphinatonickel(II). H_2ADE (50 mg) was dissolved in chloroform (10 mL), and a solution of methanol, saturated with nickel acetate (15 mL), was added. The solution was heated at reflux for 2 h. The solvent volume was lowered under reduced pressure and the crystalline product was collected. Recrystallization from dichloromethane–ethanol afforded mauve-red crystals (51 mg, 94%). Anal. Calcd for $C_{40}H_{48}N_4NiO_4$: C, 67.90; H, 7.12; N, 7.92. Found: C, 68.32; H, 6.89; N, 8.03.

$Ni_N[H_2m$-FTF6-3,2-NMe].[16] 5,15-Bis(2-methylaminoethyl)-2,18,12,18-tetraethyl-3,7,13,17-tetramethylporphine (50 mg) was dissolved in dichloromethane (50 mL) and a saturated solution of nickel acetate in methanol (15 mL) was added. The solution was heated at reflux until insertion was complete (monitored by UV/vis spectroscopy), and then water (100 mL), concentrated aqueous ammonia (5 mL), and sodium carbonate in water (10%) were added. The dichloromethane was removed under reduced pressure, and the solid collected (decantation or centrifugation). To remove all final traces of nickel salts the solid was dissolved in dichloromethane and passed through a Celite pad; the above washing and collection procedures were repeated twice using water and sodium carbonate solution. The final red dichloromethane solution was washed twice with water, dried over sodium carbonate, and filtered; the solvent was removed under reduced pressure. Following redissolution in dry dichloromethane and filtration through a Celite pad, the solution was made up to 50 mL and used in the preparation of the title "face-to-face" porphyrins with the diacid chloride derived from 5,15-bis(2-carboxyethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine (58.92 mg), as previously described.[5d] Purification of the crude product was effected by preparative TLC [SiO_2, CH_2Cl_2–Et_3N (99.5:0.5)]. Recrystallization from dichloromethane–ethanol gave red-violet microcrystals (56.2 mg, 54%). Anal. Calcd for $C_{76}H_{92}N_{10}NiO_2$: C, 73.83; H, 7.50; N, 11.33. Found: C, 73.45; H, 7.47; N, 11.11.

Insertion of Iron into Porphyrins. In a typical insertion reaction, porphyrin (10 mg) was added to a boiling solution of benzene and tetrahydrofuran (6 mL, 1:1) containing 2,6-lutidine (0.2 mL) in an inert atmosphere chamber in which the oxygen concentration was continuously monitored and maintained at less than 2 ppm. Anhydrous ferrous bromide (10 mg) was then added and the reaction mixture was heated at reflux until the insertion reaction was judged complete by UV/vis spectroscopy (1 min to 2 h). The solvents were removed under reduced pressure and the solids redissolved in toluene–methanol (9:1); purification was effected by column chromatography [Activity 1 neutral Al_2O_3, Woelm, 1 cm × 7 cm, toluene–methanol (9:1)].[19] The solvent volume was lowered to a minimum under reduced pressure, and heptane, sufficient to effect total precipitation of the product (ca. 3 mL), was added. The solid was collected and dried in vacuo.

Measurement of MCD Spectra. Reagent grade benzene or toluene distilled from sodium–benzophenone ketyl was used as the solvent for the synthetic porphyrins. Concentrations were determined by weighing or from previously reported extinction coefficients. Concentrations and cell path lengths were such that the optical densities were less than 2 throughout all absorption bands. Solutions were prepared in a drybox with rigorous exclusion of oxygen and carried to the spectrophotometers in cells fitted with gas-tight stopcocks. The possible incursion of O_2 was checked for by comparison of absorption spectra taken before and after the MCD measurement and by looking for the distinctive Soret MCD bands of products resulting from interaction of the iron porphyrins with dioxygen (vide infra). Solutions of sperm whale metmyoglobin were made up in 0.1 M sodium phosphate (pH 6.8) and reduced with a slight excess of sodium dithionite. The oxy and cabonmonoxy derivatives were prepared by gentle bubbling with the appropriate gas. Concentrations were determined by weighing, giving extinction coefficients slightly different from those reported earlier.[20] Where necessary, ligand concentrations are given in Table I.

Absorption spectra were determined on a Cary 14 spectrophotometer. MCD measurements were made on a JASCO J-40 circular dichrometer fitted with a 15-kG electromagnet. The units for MCD are magnetic molar ellipticity, $[\theta]_M$, in deg cm^2 dmol^{-1} G^{-1}. Calibration procedures for the MCD instrument have been described previously.[21] Ellipticities of dimeric porphyrins, with the exception of the mixed Fe–Ni dimer, have been divided by 2 so that a direct comparison can be made, not only between dimeric compounds, but with monomers as well.

Results and Discussion

Absorption Spectra. The absorption and Soret MCD spectral data of a number of iron(II) porphyrins, with and without axial ligands, are collected in Table I, which includes an assignment of the spin state and coordination number of each compound. While ligand binding to a four-coordinate ferrous porphyrin is accompanied by dramatic changes in the Soret region of the optical spectrum, it is not always possible to distinguish between five- and six-coordination on the basis of the observed changes. Here the major marker of coordination number is the band position, which is often separated by less than 10 nm for the five- and six-coordinate compounds. In situations where a mixture of five- or six-coordinate complexes may occur, the absorption spectrum has little diagnostic value per se.

Magnetic Circular Dichroism. Ferromyoglobin. Our application of MCD to the determination of spin state in synthetic iron(II) porphyrins is based on the observation that the shapes and signs of the MCD bands in the Soret region of hemoglobin[22,23] and myoglobin[23,24] depend on whether the iron is high-spin or low-spin. The MCD spectra of the high-spin prototype, deoxymyoglobin, and two low-spin examples, oxy- and carbonmonoxymyoglobin, in both the visible and near-UV are shown in Figure 2. The S-shaped MCD bands exhibited by the low-spin derivatives are the *A*-term bands that are characteristic for the Q and Soret π–π^* transitions of diamagnetic metalloporphyrins having approximate D_{4h} symmetry. On the other hand, the Soret MCD of deoxymyoglobin is dominated by an intense, positive MCD band which is temperature-sensitive,[24] as would be expected for the *C*-terms anticipated for a high-spin iron(II) porphyrin. In the visible region, the MCD bands of high- and low-spin forms of myoglobin are distinctive, but less dramatically so than in the Soret region. Moreover, the signs of the visible bands of high-spin iron(II) porphyrins change from the myoglobin standard when *meso*-phenyl substituents are incorporated in the porphyrin (see Figures 3 and 5). Consequently, the signs and shapes of the MCD bands in the visible region cannot generally be used as reliable markers of the spin state of iron(II) porphyrins. The Soret spectra of the low- and high-spin myoglobin examples provide a reference set to which the MCD spectra of synthetic iron(II) porphyrins can be correlated. Because the ligand binding equilibria and structural properties of Fe(TPP) with added axial ligands are well documented,[2] the MCD spectra of the Fe(TPP) system afford an additional set of reference data (Figures 3–5). The Soret MCD bands of hemoproteins that have other combinations of axial

(14) Where appropriate, we have used magnetic susceptibility data to confirm spin assignments. These were determined by the Evans[15] method, as described earlier (ref 13).

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(16) Abbreviations used: H_2TPP, *meso*-tetraphenylporphyrin; $H_2TPivPP$, picket-fence porphyrin, *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl)porphyrin; $H_2Piv_3(4CIm)P$, *meso*-tri(α,α,α-*o*-pivalamidophenyl)-β-*o*-4-(1-imidazoyl)-butyramidophenylporphyrin; H_2ADE, 5,15-bis(carbethoxymethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin. Binary porphyrins and capped porphyrins are shown in Figure 1: H_2Cap, **1a**; H_2HmCap, **1b**; $H_2PocPivP$, **2**; $H_4ClamDU$, **3**; H_4FTFDU, **4**; H_4m-FTF6-3,2-NH, **5a**; H_4m-FTF5-3,1-NH, **5b**; $H_4\beta$-FTF4-2,1-NH, **6**. Ni_N implies that nickel is inserted into the amine half of the cofacial porphyrin; Fe_A implies that iron is in the acid half; NX means that X group is on the amide nitrogens; py, pyridine; 1-MeIm, 1-methylimidazole; 1,2-MeIm, 1,2-dimethylimidazole; 1-TrIm, 1-tritylimidazole; 1-HIm, imidazole. K_B and K_B^B are the respective binding constants for the formation of five- and six-coordinate complexes.

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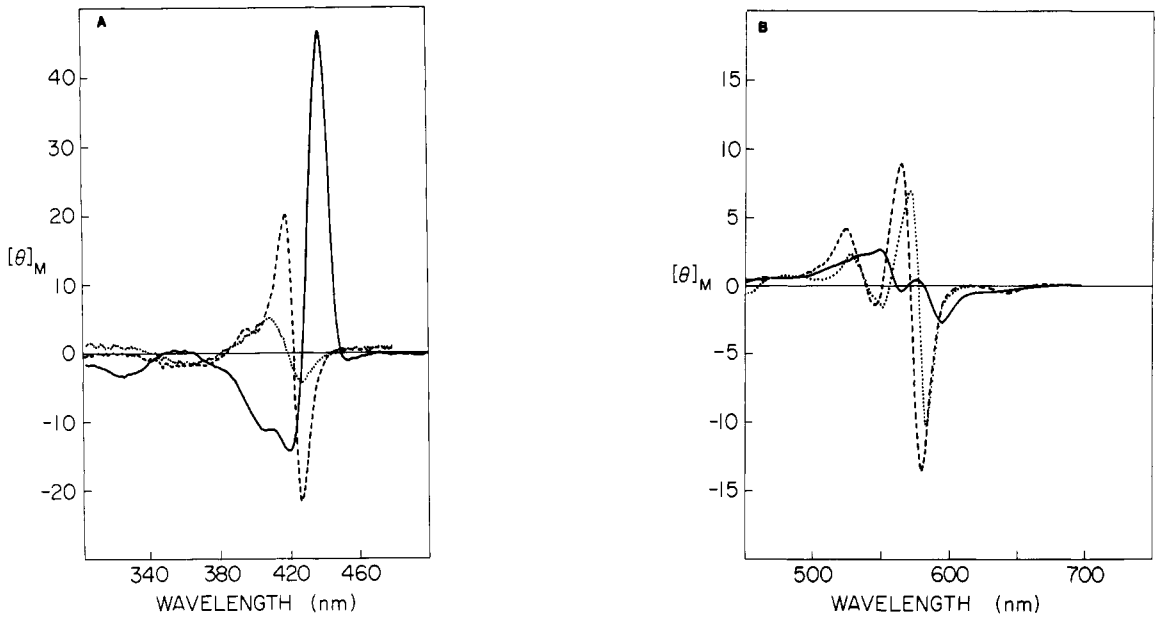

Figure 2. MCD spectra (A, Soret region; B, visible region) of Mb —; Mb + CO (1 atm) ---; Mb + O (1 atm) · · ·.

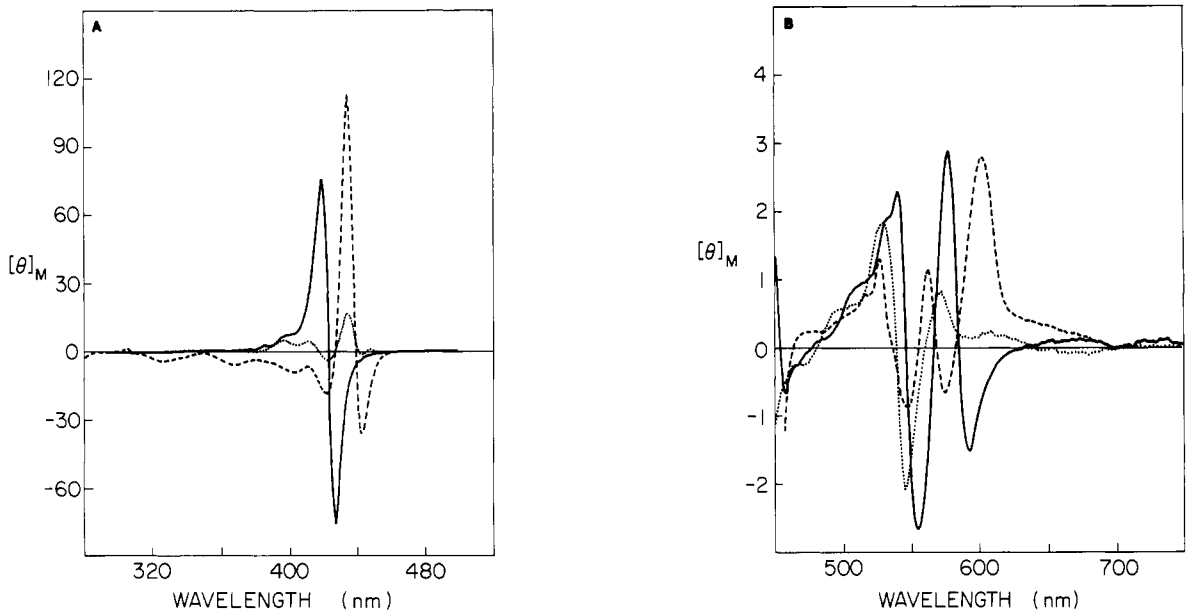

Figure 3. MCD spectra (A, Soret region; B, visible region) of Fe(TPP) in 1-MeIm (excess) + CO (1 atm) —; in 1,2-Me_2Im (0.01 M) ---; in neat toluene · · ·.

ligands, such as ferrocytochrome *c* (imidazole and cysteine)[25] and ferrocytochrome b_5–(bisimidazole)[26] are different from the classical S-shapes of oxy- and carbonmonoxymyoglobin, despite the identical spin state of the iron ($S = 0$). The ligand dependency in the low-spin examples is evident in intensity variations and in the symmetry of the Soret MCD band, which is lower than that found for oxy- and carbonmonoxymyoglobin. Similar perturbations are found in synthetic porphyrins with two nitrogenous axial ligands (vide infra).

The positive MCD Soret band observed for deoxymyoglobin (Figure 2A) is also dominant for ferrohorseradish peroxidase[22,27] and ferrocytochrome P-420.[11] The MCD spectra of high-spin iron(II) porphyrins have been explained on the basis of spin–orbit interactions between the heme iron and the porphyrin π orbitals.[22,23,28] Five-coordinate, high-spin ferrocytochrome P-450[29] constitutes another apparent departure from the deoxymyoglobin type spectrum, an observation that has been attributed[24] to a possible reversal in the sign of the spin–orbit coupling constant, as compared to that of deoxymyoglobin and deoxyhemoglobin.

It must be emphasized that the correlation of spin state and coordination number in iron(II) porphyrins with the appearance of the MCD Soret band is applicable only to those cases for which the porphyrin ring substituents are sufficiently nonperturbing, so that the porphyrin chromophore effectively retains D_{4h} symmetry. The MCD of formyl-substituted ferrohemes, such as heme *a*, for instance, are additionally complicated by strong interaction between the π orbitals of the formyl group and those of the ring. As a consequence, the MCD of *both* high- and low-spin derivatives exhibit positive MCD bands in the Soret region.[30] This con-

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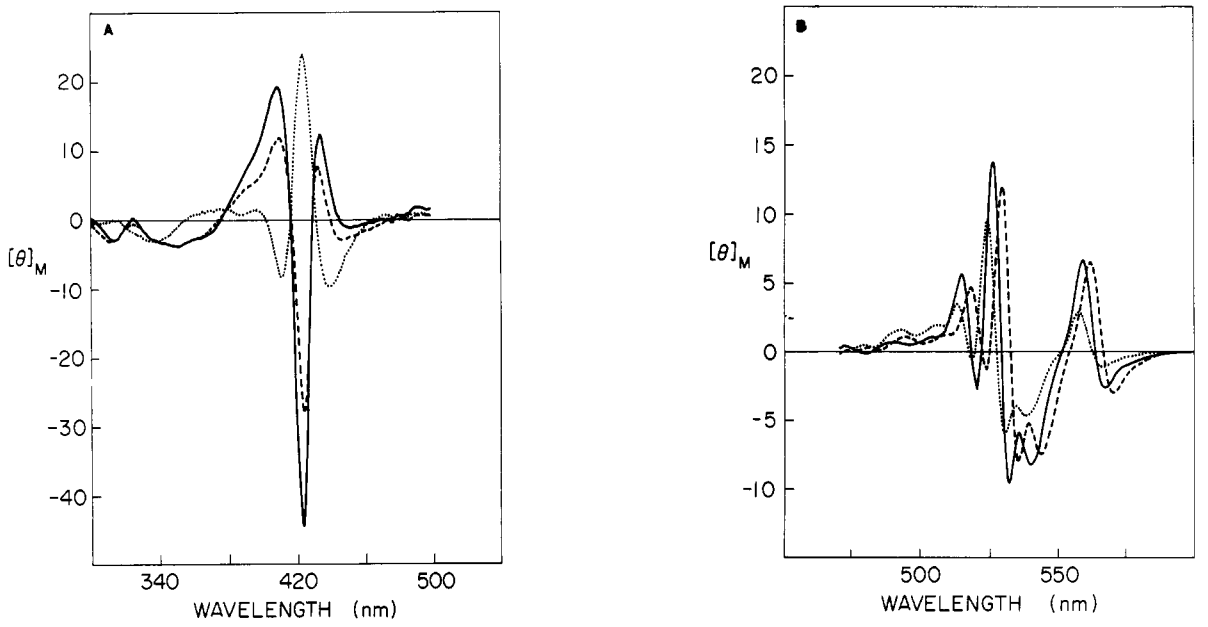

Figure 4. MCD spectra (A, Soret region; B, visible region) of Fe(TPP) in *n*-$PrNH_2$ (excess) —; in 1-MeIm (excess) ---; in pyridine (excess) • • •.

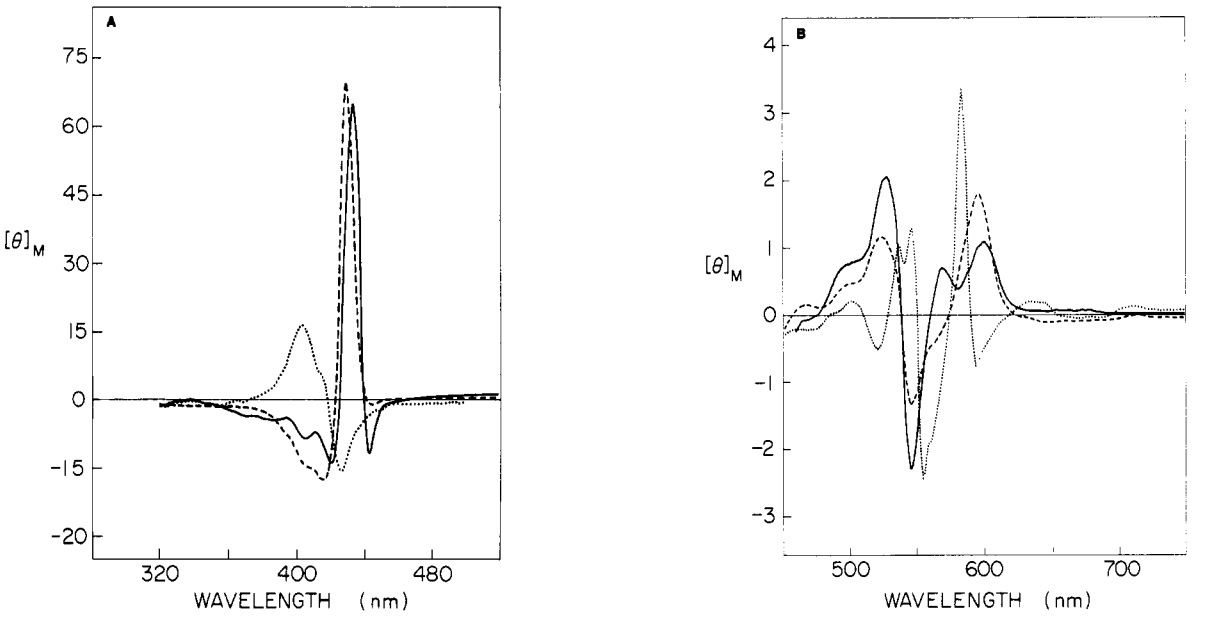

Figure 5. MCD spectra (A, Soret region; B, visible region) of Fe(TPP) in toluene–THF (1:1) —; in THF ---; in toluene + CO (1 atm) • • •.

sideration does not affect the porphyrins which are the subject of this paper.

Monomeric Iron(II) Porphyrins. The spectra of high-spin [Fe(TPP)(1,2-Me_2Im)], intermediate-spin [Fe(TPP)], and low-spin [Fe(TPP)(CO)(1-MeIm)] examples in the tetraphenylporphyrin series are shown in Figure 3. The iron(II) tetraphenylporphyrin series is the most appropriate model for relating the MCD/spin-state correlations for myoglobin to the *meso*-tetraaryl hemes discussed in this work.

In the high-spin, five-coordinate example, Fe(TPP)(1,2-Me_2Im), steric interaction between the 2-methyl group of the ligand and the porphyrin ring precludes the formation of a sixth strong ligand–iron bond.[31] This represents one form of steric control of coordination. In the capped porphyrins (vide infra), the same result is achieved by steric encumbrance covalently attached to one side of the porphyrin. The Soret MCD of Fe(TPP)(1,2-Me_2Im) ($S = 2$) (Figure 3) is dominated by a strong positive band, as was observed for deoxymyoglobin ($S = 2$), the major differences being that the negative component at longer wavelengths is weaker for deoxymyoglobin and the positive band is stronger for the synthetic porphyrin. In the visible region, the sign of the lowest energy MCD band is positive for Fe(TPP)(1,2-Me_2Im), but negative for deoxymyoglobin, thus limiting the generality of spin-state correlations to the Soret region, where uniform behavior is observed.

The MCD spectrum of unligated, four-coordinate Fe(TPP), a coordination state not found in myoglobin, is also shown in Figure 3. The spin state, $S = 1$, proposed for this heme[31] has recently been firmly established by magnetic susceptibility measurements,[32,33] by a crystal structure determination,[34] and by Mössbauer and NMR[35] spectroscopy. To our knowledge, this is

(31) Collman, J. P.; Reed, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 2048. Our more recent studies have shown that in toluene at 23.1 °C, log $K_B = 4.43$ and log $K_B^B = 0.6$, indicating that 1,2-Me_2Im does, to a certain extent, form the bis adduct with FeTPP.

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(35) Goff, H.; LaMar, G. N.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 3641.

the first MCD spectrum of an intermediate-spin iron(II) porphyrin to be reported, although the spectrum of $S = 1$ iron(II) phthalocyanine [Fe(Pc)] in dichlorobenzene has been reported by Stillman and Thomson.[36] The extent to which *C*-terms contribute to the MCD spectra of either Fe(TPP) or Fe(Pc) has yet to be determined by low-temperature MCD measurements. In the Soret region, the MCD of Fe(TPP) is characterized by the low intensity and the complexity of the bands as compared to the high- and low-spin derivatives. In the visible region, the MCD bands of Fe(TPP) are comparable in intensity to those of the ligated derivatives. These general characteristics were also observed for the unligated $S = 1$ spin state of the other porphyrins investigated.[37]

The Soret MCD band for the low-spin, six-coordinate Fe(TPP)(CO)(1-MeIm) (Figure 3) is very symmetrical, as is that of carbonmonoxymyoglobin. However, the peak values of the *A*-term bands associated with the Q_0 and Q_v transitions of Fe(TPP)(CO)(1-MeIm) are broad and of about the same amplitude, whereas in the protein the Q_0 bands have the greater magnitude. The MCD spectra of imidazole–carbonyl complexes of iron(II) porphyrins are classic[7] examples of the *A*-terms associated with a transition from a totally symmetric ground state to a degenerate excited state, for which complicating factors, such as strong, close-lying, vibrational or separate electronic transitions, are absent.

The MCD spectra of other low-spin iron(II) porphyrins do not always present such a classic appearance. While the Soret MCD of Fe(TPP)(pyrazine)$_2$ (Table I) does show a nearly symmetrical S-shaped curve, the spectra (Figure 4) exhibited by Fe(TPP)(1-MeIm)$_2$, Fe(TPP)(py)$_2$,[38] and Fe(TPP)(*n*-PrNH$_2$)$_2$ are considerably more complex. The Soret MCD of Fe(TPP)(1-MeIm)$_2$ qualitatively resembles that of its protein counterpart, ferrocytochrome b_5,[26] and that of Fe(TPP)(*n*-PrNH$_2$)$_2$. It is important to note that the positive band at about 440 nm found in the spectra of the bis(1-methylimidazole) and bis(*n*-propylamine) adducts is evidently part of their Soret MCD band system, since the curves are not altered in the presence of a very large excess of the ligands. Thus, this peak does not implicate a vestigal concentration of a high-spin, five-coordinate complex.

The point discussed in this paragraph is a matter of considerable significance concerning the use of MCD as described here. The Soret MCD of the bis(pyridine) complex is inverted as compared to those of the bis(1-methylimidazole) and bis(*n*-propylamine) adducts and, in fact, on first examination seems to resemble the band shape of the high-spin, five-coordinate complex Fe(TPP)(1,2-Me$_2$Im) (Figure 3). Since it might have been expected that all three bis-ligated complexes would exhibit similar MCD spectra, it is clear that well-defined model compounds for each type of ligand and each coordination number are needed. In the MCD spectrum of an authentic sample of a monopyridine complex, the typical positive, high-spin band appears near 432 nm (Figure 7), in contrast to 424 nm for Fe(TPP)(py)$_2$. Thus, while there is little difficulty in distinguishing between high- and low-spin states of these pyridine complexes by MCD, the principal fingerprint marker of spin state (i.e., the shape of the Soret band curve), which exists in the natural systems and in those model systems where imidazole axial bases pertain, is lost upon substitution of the ostensibly very similar axial ligand, pyridine. These considerations should be kept in mind when extending this method for spin-state determinations to ligands not included here.

In the preceding discussion, we have presented MCD spectra of ligated derivatives of Fe(TPP) in which at least one of the axial ligands is a moderate, or strong-field, σ donor. It has been shown that Fe(TPP) binds only a single, weaker field THF ligand in benzene solution ($K_{25°C} \simeq 5.8$ M^{-1}), thereby becoming five-coordinate and, apparently, high-spin.[39] More recently, the high-spin complex, Fe(TPP)(THF)$_2$, in which the iron(II) is six-coordinate and in the porphyrin plane, was isolated and characterized by a crystal structure determination and by Mössbauer and magnetic measurements. Crystal packing effects were thought to be responsible for the crystallization of this unique example of a high-spin, but six-coordinate ferrous porphyrin.[40] The Soret MCD spectrum produced by adding THF to a solution of four-coordinate Fe(TPP) in toluene (Figure 5A) exhibits the pattern which might be expected for five-coordination. A comparison with an assuredly high-spin, five-coordinate complex (Figure 7) confirms this assignment. The spectrum is not greatly changed in neat THF as might be expected, since the relative concentration of THF is little altered under the experimental conditions of the two spectra.

When CO is admitted to a solution of an iron(II) porphyrin in the presence of a good σ-donating ligand, the invariable result is that a low-spin, six-coordinate, ligand–carbonyl complex is formed.[41] However, when CO is introduced into solutions of unligated iron(II) porphyrins, Wayland et al.[42] have shown that mono- and dicarbonyl adducts are formed ($K_B = 6.6 \times 10^4$ M^{-1}, $K_B^B \simeq 140$ M^{-1}). Both the five- and six-coordinate CO complexes are diamagnetic, and thus low-spin. The Soret absorption maximum (Table I) in the optical spectrum for the solution whose MCD spectrum is shown in Figure 5 is at 418 nm [419 and 426 nm have been reported for the mono- and dicarbonyl complexes in the same solvent (toluene) as employed here[42]] and the band does not show any asymmetry. Thus, we believe the species Fe(TPP)(CO) predominates for our measurements. The general shape of the Soret MCD is consistent with that expected for a low-spin, carbonyliron(II) porphyrin (Figure 5), but does contain an unexpected shoulder between the stronger positive and negative lobes.

Ferrous Capped Porphyrins. The series of porphyrins based on the capped porphyrin and the picket-fence porphyrin have contributed to an understanding of the interaction of molecular oxygen with hemoproteins. In these model compounds, a degree of control of coordination has been achieved. In the presence of excess axial base, either (a) a solely five-coordinate porphyrin is produced [e.g., Fe(Cap), **1a**], for which the binding of a second bulky axial ligand is precluded by steric encumbrance, but added oxygen or carbon monoxide is sufficiently small to coordinate to the iron within the cavity created by the cap,[3b,c,43] or (b) a six-coordinate complex is formed [Fe(PTivPP)], but dissociation to form a five-coordinate complex occurs preferentially from the picketed side of the porphyrin, resulting in coordination of added carbon monoxide or oxygen within the enclosure of the picket fence.[3a] Coordination of oxygen within these protecting cavities slows the rate of irreversible oxidation of the iron and allows for the study of dioxygen complexes under ambient conditions.

Recently, the "pocket" porphyrin, Fe(PocPivP), **2** (Figure 1), has been synthesized and the oxygen and carbon monoxide affinities have been determined. The pocket in this model is designed to allow an unhindered and, hopefully, nondisordered, bent FeO_2 unit to form, but to provide steric encumbrance sufficient to bend or tilt the normally linear FeCO moiety off the porphyrin perpendicular. This represents a further refinement in structural design to achieve the desired control of coordination and is directed at examining the effect of steric distortion on the affinity of the heme for carbon monoxide and at obtaining better or more relevant structural information for dioxygen and carbon monoxide complexes of iron(II) porphyrin models of hemoproteins.[18]

While MCD has been used to investigate the coordination of iron in the picket-fence family of porphyrins,[13] it has not hitherto

(36) Stillman, M. J.; Thomson, A. J. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 790.

(37) Square-planar hemes are very sensitive to the incursion of adventitious ligands which either result in the formation of small amounts of ligated species or, in the case of oxygen, in the formation of, for instance, [Fe(TPP)]$_2$O. We have repeated our MCD measurements on different samples of Fe(TPP) and find that, while the MCD in the Q band region can be satisfactorily reproduced, the details of the MCD Soret band structure are subject to slight variation in intensity.

(38) We have confirmed the diamagnetic nature of this bis(pyridine) complex by both NMR and magnetic susceptibility measurements.

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Table I. Absorption and Soret MDC Data for Selected Iron(II) Porphyrins

porphyrin	ligand(s)	coord. no.	spin state	Soret absorption,[b,c] λ_{max} (mME)			
Fe(TPP)	*a*	4	1	400 (sh) (48.7)	418 (83.3)	436 (75.4)	
	a	4	1	400 (sh) (64.7)	419 (107.4)	442 (79.5)	
Fe(PocPivP)		4	1		420 (143.9)	441 (129.6)	
Fe(Cap)		4	1	401 (sh) (54.2)	421 (98.5)	446 (95.3)	
Fe(HmCap)		4	1		428 (96.2)	449 (sh) (43.9)	
	2.0 M 1-MeIm	6	1		429 (171.2)		
	3.0 M py	6	1		422 (sh) (125.4)	429 (150.0)	
Fe_2(FTFDU)		4, 4	1, 1		*i*	↕	
Fe_2(ClamDU)		4, 4	1, 1	413	440	↓	
Fe_2(*m*-FTF6-3,2-NH)		4, 4	1, 1	364 (sh) (20.7)	419 (56.9)	452 (sh) (26.8)	
Fe(TPP)	1,2-Me_2Im	5	2	368 (2.18)	416 (sh) (51.3)	437 (248.8)	
Fe(ADE)	2-MeIm	5	2			431 (180.8)	
Fe(PocPivP)	2.0 M 1-MeIm	5	2			439 (320.1)	
	0.03 M 1-HIm	5	2			438 (224.6)	
	pyrazine	5	2			431 (151.5)	
Fe(Cap)	2 M 1-MeIm	5	2		414 (sh) (49.5)	439 (217.6)	
	2 M py	5	2			435 (200.0)	
Fe(HmCap)	0.01 M 1-MeIm	5	2			434 (126.9)	
Fe_2(FTFDU)	1-TrIm	5, 5	2, 2	428		↕	
	1-MeIm	5, 5	2, 2	428			
Fe_2(ClamDU)	1-TrIm	5, 5	2, 2	430		↓	
Fe_2(*m*-FTF6-3,2-NH)	0.01 M 1-TrIm	5, 5	2, 2			429 (64.2)	
FTF6	0.03 M 1,2-Me_2Im	5, 5	2, 2			429 (78.1)	
	0.01 M py	5, 5	2, 2			425 (75.0)	
	0.01 M 1-MeIm	5, 5	2, 2			430 (78.1)	
Fe_2(β-FTF4-2,1-NH)	0.03 M 1-HIm	5, 5	2, 2		361 (37.2)	409 (71.2)	
	0.02 M 1-MeIm	5, 5	2, 2		360 (27.6)	405 (40.0)	
	0.4 M 1-MeIm	5, 5	2, 2		360 (33.0)	405 (54.0)	
Fe(PocPivP)	50% THF	5	2		399 (sh) (96.4)	430 (289.4)	
Fe(TPP)	50% THF	5[d]	2		400 (sh) (55.3)	431 (200.0)	
	neat THF	5[d]	2		402 (sh) (53.7)	427 (248.8)	
Fe_2(β-FTF4-2,1-NH)	neat THF	*d*			331 (21.3)	383 (43.5)	
Fe(TPP)	1-MeIm	6	0		406 (sh) (50.0)	427 (250.0)	
	pyrazine	6	0			427 (247.0)	
	n-$PrNH_2$	6	0		405 (sh) (57.4)	426 (286.8)	
	py	6	0			424 (170.3)	475 (10.8)
	0.01 M 1-TrIm	6	0		407 (sh) (53.5)	426 (310.8)	
Fe(ADE)	1-MeIm	6	0			423 (240.0)	
Fe(PocPivP)	1.0 M *n*-$PrNH_2$	6	0			440 (217.6)	
Fe(HmCap)	0.01 M *n*-$PrNH_2$	6	0			425 (191.5)	
Fe_2(FTFDU)	pyrazine	6, 6	0, 0			*i*	
	py + 1-TrIm	6, 6	0, 0		418	↕	
Fe_2(ClamDU)	1-MeIm	6, 6	0, 0		426	↓	
Fe_2(β-FTF6-3,2-NH)	0.01 M 1-MeIm + 0.01 M py	*e*				419 (88.2)	
Fe_2(β-FTF6-3,2-NH)	1.0 M 1-MeIm	*e*				416 (44.1)	468 (sh) (12.4)
Fe_2(β-FTF4-2,1-NH)	0.02 M 1-MeIm + 0.01 M py	3			360 (8.0)	406 (67.7)	
Fe(Cap)	0.1 M *n*-$PrNH_2$	5,6	2, 0		417 (sh) (77.1)	438 (144.3)	
	1.0 M *n*-PrNH	5, 6	2, 0			427 (200.0)	
Fe_2(*m*-FTF6-3,2-NH)	0.03 M 1-HIm	5, 6	2, 0			424 (76.5)	
Fe_2(*m*-FTF6-3,1-NH)	0.1 M 1-MeIm	5, 6	2, 0		352 (sh) (21.9)	420 (69.3)	422 (sh) (45.5)
Fe(TPP)	CO	5	0			418 (140.0)	
	1-MeIm + CO	6	0			427 (335.6)	
Fe(ADE)	1-MeIm + CO	6	0			419 (182.6)	
Fe(PocPivP)	1-MeIm + CO	6	0			427 (208.9)	
Fe(Cap)	1M*n*-$PrNH_2$ + CO	6	0			424 (307.7)	
Fe(HmCap)	0.01 M *n*-$PrNH_2$ + CO	6	0			423 (258.9)	
Fe_2(FTFDU)	1-TrIm + CO	6, 6	0, 0	420		↕	
Fe_2(ClamDU)	1-MeIm + CO	6, 6	0, 0	419			
	1-TrIm + CO	6, 6	0, 0	418		↓	
Fe_2(*m*-FTF6-3,2-NH)	0.01 M 1-TrIm + CO	6, 6	0, 0			421 (90.2)	
	0.03 M 1,2-Me_2Im + CO	6, 6	0, 0			420 (112.8)	
Fe_2(*m*-FTF5-3,1-NH)	1-MeIm + CO	6, 6	0, 0			*i*	
Fe_2(β-FTF4-3,1-NH)	0.02 M 1-MeIm + CO	*f*			325 (16.4)	390 (87.1)	413 (sh) (25.4)
Fe(PocPivP)	1-MeIm + O_2	6	0			424 (80.4)	
Fe[Piv_3(4ClmP)P]	attached Im + O_2	6	0		372 (3.3)	426 (12.9)	
Fe_2[*m*-FTF6-3,2-NH]	1-MeIm/O_2	*g*				417 (63.6)	
Fe_2[β-FTF5-3,1-NH]	1-MeIm/O_2	*g*		341 (47.6)	386 (57.5)	442 (sh) (18.3)	
Fe(TPP)	μ-oxo	5		409 (85.4)		↕	

[a] Separate determinations. [b] ε and $[\theta]_M$ values subject to ±20% error. [c] ε and $[\theta]_M$ values reported on a per heme basis. [d] Model spectra of six-coordinate THF complexes not established. [e] Exact ligation and spin states uncertain. [f] Appears to contain some five-coordinate,

been applied to studies of capped or pocket iron porphyrins. As described below, MCD can provide useful information for determining what ligands can or cannot be admitted into the cavities of these metalloporphyrins. Comparison of the Soret MCD spectra of the aryl-capped porphyrins with the analogous spectra of noncapped, monomeric, iron porphyrins shows that the bands for the former are generally of lesser intensity than for the latter. This reduced band intensity is also pronounced in the cofacial porphyrin series (vide infra) and may be the result of electronic interactions between the porphyrin rings (exciton coupling), as well as steric constraints on the porphyrin macrocycle, especially in the capped series.

The MCD spectrum of Fe(Cap) in the presence of 0.1 M *n*-propylamine shows that a five-coordinate, high-spin species predominates (Figure 6). The effect of the cap is dramatic, since here, with a porphyrin-to-ligand ratio approximating 1:2000, the ligand concentration is more than 100 times that required to effectively give only the six-coordinate complex in cases where the steric hindrance is absent. That a small amount of a low-spin species is also present is suggested by a more intense negative peak at 425 nm and less intense positive peak at 438 nm than is observed with 1-methylimidazole (Figure 7), which is known to form only a five-coordinate complex.[3b] In 1.0 M *n*-propylamine solutions, conversion to the six-coordinate complex is greater, but is not complete (Figure 6). The MCD spectrum tends toward that of the six-coordinate model, Fe(TPP)(*n*-$PrNH_2$)$_2$ (Figure 4).

The related ferrous porphyrin, Fe(HmCap), **1b**, is capable of providing a larger cavity for access of axial ligands to the iron

visible absorption λ_{max} (mME)				Soret MCD λ_{max} ($[\theta]_M$)[b,c]						
537 (9.55)					397 (+4.9)	412 (+4.2)	423 (−4.4)	435 (+16.5)		
537 (10.1)				378 (−3.2)	396 (+3.0)	412 (+6.2)	423 (−3.3)	445 (+16.0)		
538 (21.0)				380 (−0.9)	400 (sh) (+0.6)	415 (+3.1)	425 (−2.7)	439 (+10.2)		
537 (11.8)				381 (−3.3)		414 (+12.1)	424 (−5.1)	432 (+2.0)	441 (−7.6)	450 (+7.7)
538 (9.22)				384 (−1.0)	398 (sh) (+0.9)	415 (+5.0)	426 (−7.7)	440 (10.0)		
536 (14.1)	565 (5.17)					413 (+10.0)	427 (−2.5)	431 (+0.7)	439 (−31.7)	
530 (18.7)	557 (sh) (7.86)				406 (+3.6)		427 (+23.0)	435 (−23.3)	448 (−3.6	
	i			384 (−5.6)	393 (+5.0)	405 (−13.8)	416 (+7.8)	435 (+29.8)		
537	560 (sh)			384 (−5.6)	395 (+5.6)	406 (+6.1)	414 (+5.8)	424 (−6.1)	437 (+20.0)	
549 (7.07)	586 (5.47)			387 (−2.3)			416 (+6.1)	432 (sh) (+0.8)	447 (−2.7)	463 (+1.9)
534 (7.10)	565 (8.09)	609 (3.32)					422 (−18.6)	435 (+110.6)	443 (−35.0)	
535 (4.46)	554 (6.25)						418 (−17.0)	432 (+72.0)	445 (−5.0)	
541 (21.4)	563 (19.6)	618 (sh) (8.85)					425 (−7.7)	438 (+44.0)	449 (−7.7)	
541 (14.3)	561 (13.6)						425 (−2.9)	438 (+24.0)	449 (−6.0)	
533 (14.8)	618 (sh) (2.77)						422 (−6.0)	439 (+15.4)		
540 (8.82)	563 (7.35)	613 (2.66)					425 (−20.6)	439 (+89.6)	449 (−9.8)	
537 (6.00)	565 (3.41)	615 (2.00)					424 (−30.0)	440 (+80.0)		
537 (10.3)	566 (5.62)						426 (−19.6)	439 (+45.3)	452 (−1.1)	
	i						415 (−17.9)	433 (+92.3)	449 (−6.5)	
	i						406 (−11.1)	432 (+81.2)	446 (−12.3)	
536	565						420 (−11.4)	434 (+69.6)	450 (−6.2)	
550 (5.64)	591 (4.60)						422 (−0.9)	436 (+6.7)	451 (−0.1)	
558 (6.31)							416 (sh) (+0.9)	432 (+7.8)	446 (−0.8)	
542 (9.08)	580 (6.89)					392 (−1.0)	414 (+0.4)	432 (+6.2)	451 (−0.8)	
548 (6.21)	582 (5.24)						414 (+1.2)	430 (+4.5)	447 (−0.4)	
550 (5.00)				315 (−1.7)	335 (+0.4)	357 (−1.7)	384 (sh) (−1.0)	416 (+6.4)		
528 (sh) (2.90)	559 (3.87)			315 (−2.0)	336 (+1.4)	361 (−2.5)	393 (−3.0)	414 (+10.7)		
526 (sh) (3.44)	559 (5.34)			313 (−2.5)	335 (+1.6)	360 (−2.5)	394 (−4.6)	414 (+13.3)		
538 (18.6)							418 (−6.9)	432 (+26.9)		
540 (12.7)							421 (−13.9)	434 (+64.0)	443 (−11.7)	
540 (9.67)							416 (−17.6)	430 (+68.9)	444 (−1.2)	
530 (sh) (3.57)	568 (4.43)				330 (−1.5)	369 (−2.6)	386 (+0.9)	402 (+4.9)	440 (+1.2)	
535 (20.3)	565 (4.82)						409 (+11.8)	425 (−27.5)	447 (−2.9)	
525 (35.4)	559 (13.8)							422 (+54.4)	432 (−44.8)	
531 (25.8)	562 (5.45)						409 (+19.1)	424 (−43.4)	434 (+12.0)	452 (−1.5)
528 (18.3)	560 (3.14)						411 (−8.3)	424 (+23.7)	439 (−10.0)	
533 (27.1)	563 (6.58)						408 (+13.7)	424 (−26.5)	431 (+15.0)	445 (−3.0)
532	562						403 (+3.4)	418 (−8.4)	427 (+9.2)	445 (−3.4)
540 (22.0)	581 (sh) (7.34)								426 (+10.0)	443 (−18.0) 460 (+2.0)
531 (18.0)	559 (5.37)						409 (+10.6)	424 (−23.3)	433 (+6.7)	
	i						413 (+42.4)	429 (−38.4)		
	i						416 (+39.7)	438 (−18.2)		
534	565						411 (+22.6)	423 (−42.4)	433 (+7.7)	448 (−4.9)
539 (7.95)	580 (6.32)						420 (+8.9)	436 (−3.7)		
546 (6.96)	576 (5.97)					352 (−7.8)	407 (+2.9)	430 (−2.0)	475 (−0.4)	
520 (7.25)	556 (12.9)	590 (sh) (3.75)				374 (−0.7)	409 (+8.3)	427 (−2.5)		
541 (10.0)								424 (−16.4)	438 (+5.2)	
532 (19.4)	563 (4.84)						411 (+10.0)	426 (−32.6)	438 (+21.3)	453 (−1.3)
571 (10.8)							414 (+3.3)	427 (−4.7)	444 (+7.1)	459 (−1.2)
550 (6.07)						360 (−0.9)	403 (+2.9)	427 (−2.2)	444 (+5.0)	
516 (8.64)	551 (8.22)	590 (4.57)	608 (3.23)				404 (+16.5)	415 (sh) (+5.9)	427 (−15.0)	
542 (12.3)	580 (4.50)							418 (+77.4)	426 (−73.0)	
544 (9.09)								414 (+27.0)	425 (−23.2)	
519 (16.6)								422 (+12.1)	433 (−11.9)	
542 (13.8)	584 (sh) (4.79)							420 (+64.0)	429 (−62.0)	
544 (16.7)	579 (7.69)							419 (+50.0)	429 (−50.0)	
536	567 (sh)							416 (+88.0)	424 (−86.4)	
535								413 (+72.0)	422 (−79.0)	
537								414 (+57.6)	420 (−54.8)	
556 (sh) (5.45)								417 (+9.3)	430 (−8.3)	
519 (7.59)	557 (7.32)							415 (+9.9)	428 (−8.9)	
							350 (−2.0)	415 (+10.5)	428 (−9.6)	
550 (8.21)					337 (−1.3)	386 (+11.9)	395 (−8.8)	411 (+1.0)	420 (−2.6)	
559 (11.7)								422 (+2.5)	437 (−1.9)	
548 (1.20)	585 (sh) (0.40)						407 (+1.3)	417 (−1.1)		
573 (5.11)							406 (+4.0)	430 (−3.2)	491 (−0.5)	
572 (14.0)	631 (sh) (6.67)				320 (+0.9)	349 (−2.9)	389 (+3.1)	451 (−1.1)		
570 (7.60)	611 (3.38)						405 (+18.6)	430 (−14.1)		

high-spin heme. [g] Nature of the compound(s) produced when O_2 is added to a 1-MeIm containing solution of this heme is (are) unknown. [h] Center of structured bands. [i] Not recorded.

center, as has been confirmed by the measurement of K_B and K_B^B values for the ligation of several nitrogen donor bases, including *n*-propylamine with Fe(HmCap).[3b] MCD provides a graphic illustration of this result. For example, the MCD spectrum of Fe(HmCap) in the presence of 0.01 M *n*-propylamine (Figure 8) (metalloporphyrin to ligand ratio approimately 1:400) has a shape identical with that observed for Fe(TPP)(*n*-$PrNH_2)_2$ (Figure 4), indicating complete formation of the six-coordinate complex, a result that is expected from analysis of the equilibrium binding constants for *n*-propylamine to this metalloporphyrin. Recalling that in the presence of 1.0 M *n*-propylamine Fe(Cap) is still not fully six-coordinated (Figure 6), it is of interest to note that the pocket porphyrin, **2**, exhibits a six-coordinate Fe(TPP)(*n*-$PrNH_2)_2$-type spectrum in the presence of 1.0 M *n*-propylamine (Figure 10). This indicates that a second *n*-propylamine ligand has greater access to the iron center of Fe(PocPivP) than to that of Fe(Cap). In 0.01 M *n*-propylamine, however, a mixture of five- and six-coordinate complexes exists for Fe(PocPivP), demonstrating less access for it than for Fe(HmCap). Magnetic susceptibility studies of Fe(PocPivP) confirm this change in spin state: at a ligand-to-porphyrin ratio of 200, μ_{eff} = 3.77 BM, but in the presence of a 1000-fold excess of *n*-propylamine, a diamagnetic complex results. A typical six-coordinate, carbonyl complex spectrum is produced with Fe(PocPivP) in excess 1-methylimidazole under CO (Figure 11).

That Fe(Cap) forms only five-coordinate complexes in the presence of ligands of bulk similar to, or greater than, 1-methylimidazole or pyridine is well documented.[3b] This property

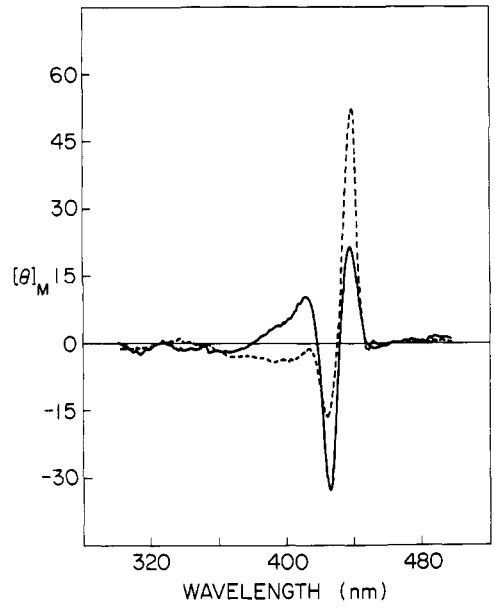

Figure 6. MCD spectra in Soret region of Fe(Cap) in 1.0 M *n*-$PrNH_2$ —; in 0.1 M *n*-$PrNH_2$ - - -.

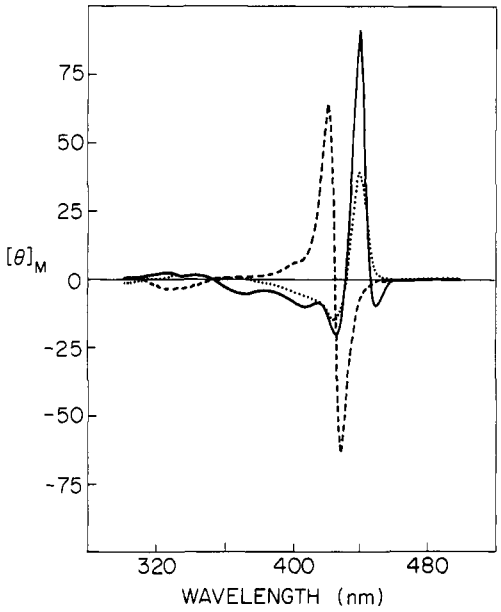

Figure 7. MCD spectra in Soret region of Fe(Cap) in 2 M 1-MeIm —; in 1 M *n*-$PrNH_2$ + CO (1 atm) - - -; in pyridine (excess) · · ·.

is further illustrated by the appropriate MCD spectra (Figure 7, Table I). CPK models suggest and MCD demonstrates that Fe(PocPivP) also forms only five-coordinate complexes in the presence of large excesses of ligands 1-methylimidazole, pyrazine, and imidazole (Figures 10 and 11). The MCD of Fe(PocPivP) in 1:1 THF–toluene (Figure 11) is, hence, interpreted as being representative of a five-coordinate, high-spin (μ_{eff} = 5.1 BM, S = 2) complex. However, Fe(HmCap) not only forms five-coordinate complexes with 1-methylimidazole and pyridine but also forms unusual intermediate-spin metallo complexes where a second ligand is thought to bind to the iron center in a five-coordinate complex through the side of the cap in a nonaxial fashion.[3b] The Soret and visible region MCD spectra of the three known examples of intermediate-spin complexes in the Fe(HmCap) series are shown in Figure 9. Although there is correspondence between the shapes of the MCD bands observed for unligated Fe(HmCap) (S = 1) and unligated Fe(TPP) (S = 1) (Figure 3), the large affinity of these species for adventitious ligands should be kept in mind. In the visible region, the spectra of the 1-methylimidazole and pyridine intermediate-spin complexes are nearly identical and are more similar in shape to ferrous porphyrin complexes coordinated

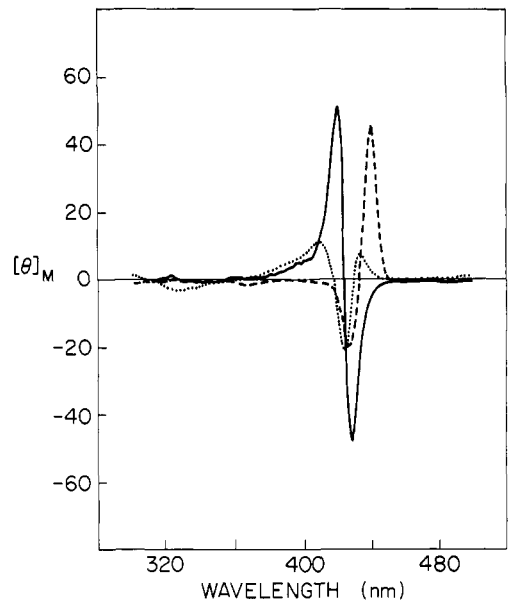

Figure 8. MCD spectra in Soret region of Fe(HmCap) in 0.01 M *n*-$PrNH_2$ + CO (1 atm) —; in 0.01 M 1-MeIm - - -; in 0.01 M *n*-$PrNH_2$ · · ·.

with two imidazole-type, nitrogen donor ligands than any other case. In the Soret region, the bands are not akin to any standard spectrum, but the weak negative peak at 427 nm for the 1-methylimidazole case may implicate a small fraction of normal (S = 0) six-coordinate complex. The MCD spectra thus provide evidence, in addition to the magnetic[3b] and resonance Raman data[44] already reported, for the unique nature of these compounds which are, as yet, not structurally characterized.

"Face-to-Face" Porphyrins. The synthesis of cofacial porphyrins, stimulated by a search for multielectron redox catalysts,[5] has added further dimensions to the coordination chemistry of iron porphyrins. By analogy with the discussion of MCD applications to capped iron porphyrins, MCD offers a simple way of examining the structural characteristics of binary, cofacial porphyrins in terms of answering questions concerning which ligands can be admitted into the cofacial cavity to form bis-five-, bis-six-coordinate or mixed five-coordinate/six-coordinate, binary metalloporphyrins. The free-base forms of the cofacial porphyrins studied in this work are of four types, as shown in Figure 1, and each type has been the subject of earlier documentation.[5] In addition to the effects that ligand binding have on the MCD spectra of iron "face-to-face" porphyrins, perturbations on the spectra of the parent monomers, derived from possible electronic effects imposed by the proximity of the porphyrin rings (exciton coupling), are to be expected. These effects are reflected in absorption spectroscopy, primarily by band shifts and band broadening in the spectra of the binary porphyrins as compared to those of the monomers. In MCD, these effects apparently obscure exact additivity of the monomeric spectra, but the main features associated with correlations between band shape and spin-state axial ligation remain unaffected. Here we are concerned with the information that can be derived from MCD about the ligation state of the metal.

Because the pattern and type of peripheral substitution in the cofacial porphyrins examined here are variable, electronic and structural effects are expected to cause differences in the MCD spectra. Standards are provided for the β-pyrrole-linked, binary porphyrin complex Fe_2(β-FTF4-2,1-NH), **6**, by myoglobin and for the meso-aryl-linked examples, **3** and **4**, by Fe(TPP). We measured a set of spectra for Fe(ADE) (Figure 15) to provide standards for the meso-alkyl-linked, cofacial porphyrins **5a** and **5b**. Comparison of these curves with the corresponding myoglobin (Figure 2) and tetraphenylporphyrin (Figures 3 and 4) analogues

(44) Linard, J. E.; Shriver, D. F.; Basolo, F. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 1741.

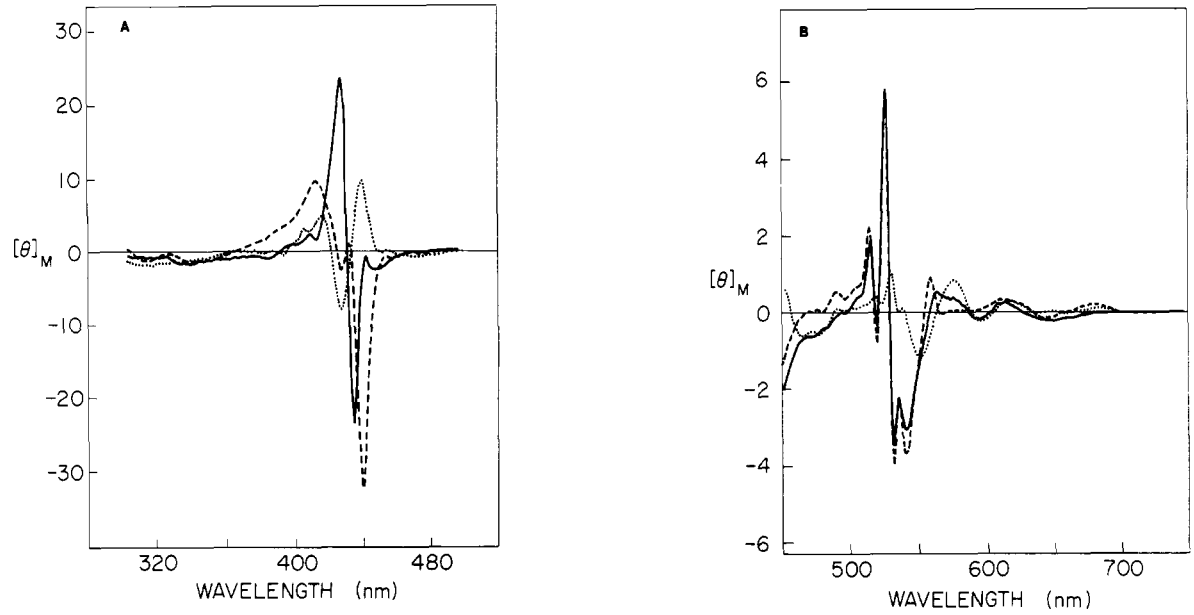

Figure 9. MCD spectra (A, Soret region; B, visible region) of Fe(HmCap) in pyridine (excess) —; in 2.0 M 1-MeIm - - -; in neat toluene · · ·.

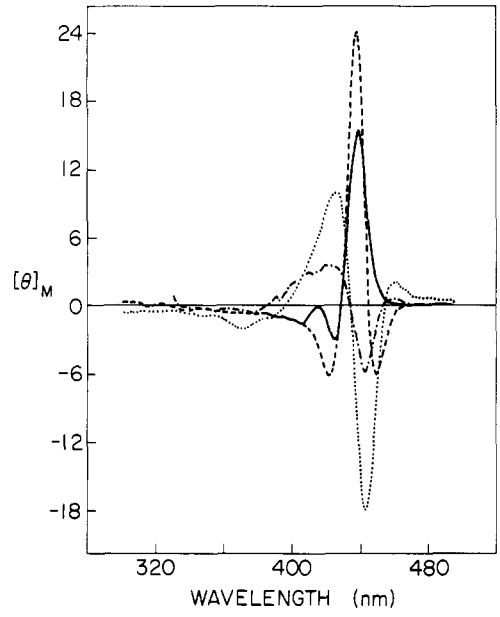

Figure 10. MCD spectra in Soret region of Fe(PocPivP) in pyrazine (excess) —; in 0.03 M 1-HIm - - -; in 0.01 M *n*-$PrNH_2$ ·····; in 1.0 M *n*-$PrNH_2$ · · ·.

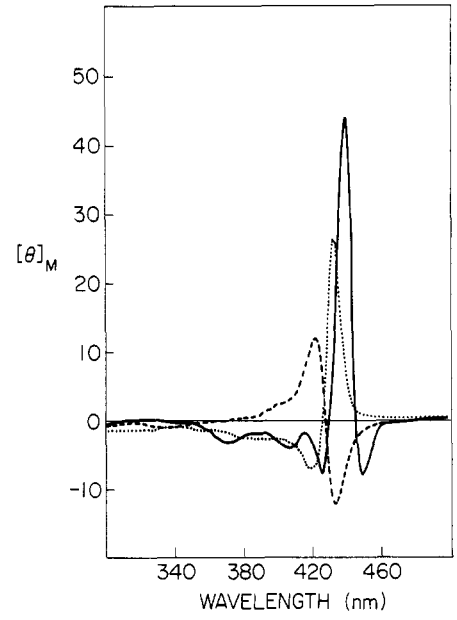

Figure 11. MCD spectra in Soret region of Fe(PocPivP) in 1-MeIm (2.0 M) —; in 1-MeIm (excess) + CO (1 atm) - - -; in toluene–THF (1:1) · · ·.

shows that the Soret MCD band shapes characteristic of high- and low-spin states with imidazole axial ligands are maintained throughout the series. The magnitudes of the MCD bands of the adducts of Fe(ADE) are intermediate between those of myoglobin and Fe(TPP) and the peak positions are somewhat blue shifted. There are apparently no pronounced effects in the MCD associated with distortions in the monomer macrocycle, owing to possible steric crowding[5d,45] around the meso-alkyl positions.

In toluene solutions of the very bulky ligand 1-tritylimidazole, Fe_2(ClamDU), **3**,[5c] Fe_2(FTFDU), **4**,[5c] and Fe_2(*m*-FTF6-3,2-NH), **5a**,[5d] all form five-coordinate complexes (Figures 12 and 16). Ligands of less bulk than 1-tritylimidazole are able to pry open the cavities of Fe_2(ClamDU). In the presence of excess 1-methylimidazole, Fe_2(FTFDU) remains five-coordinate, but Fe_2(ClamDU) (Figure 13) gives a spectrum resembling the six-coordinate model, Fe(TPP)(1-MeIm)$_2$ (Figure 4). The cis ring juncture in the "clamshell" porphyrin, **3**, apparently permits the ligation of two 1-methylimidazole ligands, whereas the trans configuration of Fe_2(FTFDU) does not. Examination of CPK models shows these findings are reasonable. From the MCD spectra of Fe_2(*m*-FTF6-3,2-NH), shown in Figure 17, it is evident that a concentration of imidazole and 1-methylimidazole can be chosen such that either one or two ligands can be forced into the cavity. In the presence of 0.03 M imidazole, one of the iron(II) centers remains high-spin (positive MCD band at 444 nm), while the other becomes low-spin and six-coordinate (positive band at 414 nm; both high- and low-spin forms contribute to the negative band at 427 nm). 1-Methylimidazole is a bulkier ligand than imidazole, but it is apparent from the MCD spectrum (Figure 17) that, at sufficiently high ligand concentrations (1 M, porphyrin-to-ligand ratio approximately 1:2 × 10^4), more than one 1-methylimidazole ligand will enter the cavity.

We have found, unfortunately, that the five-atom-bridged, meso-linked Fe_2(*m*-FTF5-3,1-NH), **5b**,[5d] is not very soluble in benzene or toluene and that it is extremely sensitive to irreversible oxidation by molecular oxygen, even at the very low oxygen

(45) (a) Abraham, R. J.; Jackson, A. H.; Kenner, G. W.; Warburton, D. *J. Chem. Soc.* **1963**, 853. (b) Grigg, R.; Shelton, G.; Sweeney, A.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1789.

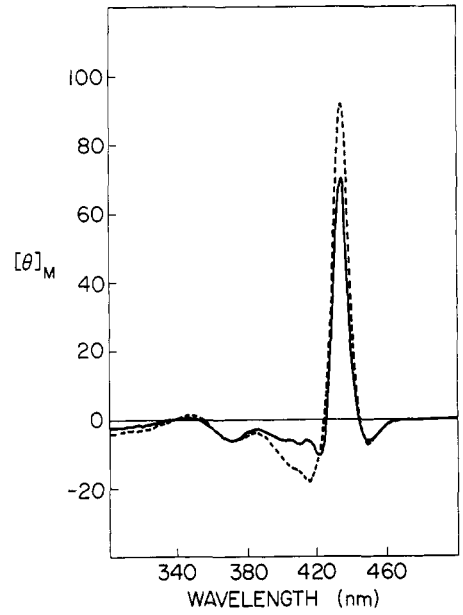

Figure 12. MCD spectra in Soret region of Fe_2(ClamDU) in 1-TrIm (excess) —; Fe_2(FTFDU) in 1-TrIm (excess) - - -.

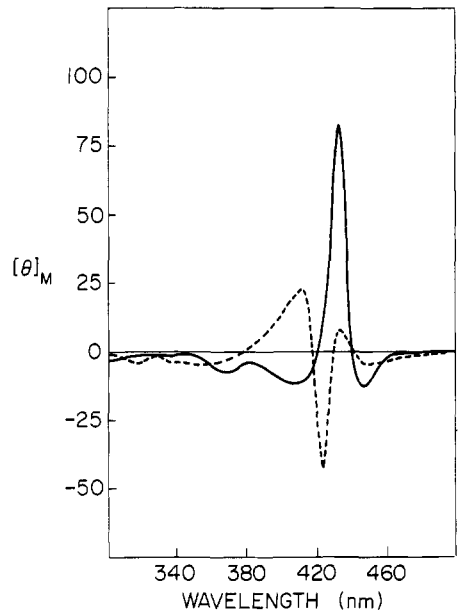

Figure 13. MCD spectra in Soret region of Fe_2(FTFDU) in 1-MeIm (excess) —; Fe_2(ClamDU) in 1-MeIm (excess) - - -.

concentrations attainable in our inert atmosphere chamber. The two valid spectra we were able to obtain are shown in Figure 18. The Soret MCD of Fe_2(*m*-FTF5-3,1-NH) in the presence of 0.1 M 1-methylimidazole indicates that, at this ligand concentration, a state of mixed five–six ligation exists.

The Fe_2(*β*-FTF4-2,1-NH), **6**, series also presented solubility problems which could, however, be circumvented by the addition of a small amount of tetrahydrofuran. Since stronger field N-donor ligands were used, the presence of the weakly coordinating THF in the solutions does not result in any spectral ambiguities. The spectra that we were able to obtain from the iron derivatives of this porphyrin are shown in Figures 20 and 21. From the Soret MCD spectra it is clear that at moderate concentrations (porphyrins-to-ligand ratio approximately 1:500) of imidazole and 1-methylimidazole, the equilibrium binding constants are such that the bis-five-coordinate complex is effectively the only species present (Figures 20 and 21). Thus, the cavity of this porphyrin is, indeed, smaller than that of Fe_2(*m*-FTF6-3,2-NH), which, in the presence of an identical concentration of imidazole (0.03 M), showed mixed five–six-coordinate ligation (Figures 21 and 17).

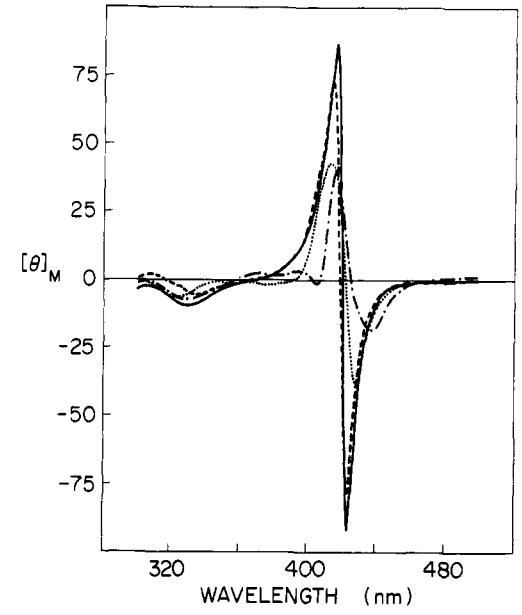

Figure 14. MCD spectra in Soret region of Fe_2(FTFDU) in 1-TrIm (excess) + CO (1 atm) —; Fe_2(ClamDU) in 1-MeIm (excess) + CO (1 atm) - - -; Fe_2(FTFDU) in 1-TrIm (excess) + pyrazine (excess) ·····; in pyrazine (excess) · · ·.

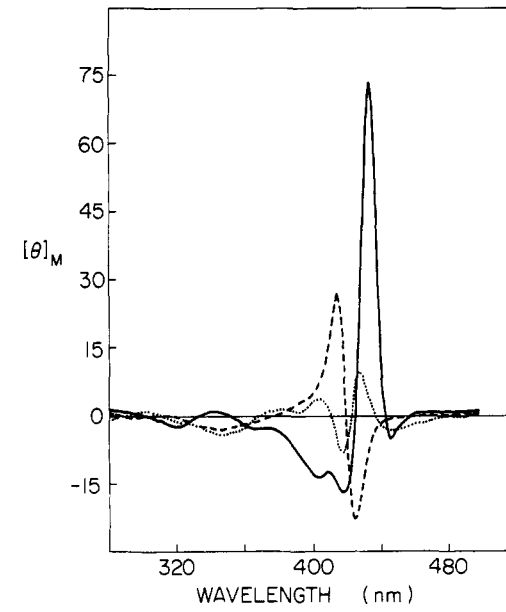

Figure 15. MCD spectra in Soret region of Fe(ADE) in 2-MeIm (excess) —; in 1-MeIm (excess) + CO (1 atm) - - -; in 1-MeIm (excess) · · ·.

The MCD spectra of the several "face-to-face" porphyrins were obtained in the presence of pyrazine, a ligand which has the potential for binding simultaneously to both interior binding sites. The Soret MCD spectrum of a five-coordinate, pyrazine complex, Fe(PocPivP)(pyrazine) (Figure 10), closely resembles the typical spectrum for a five-coordinate, imidazole base complex, and the Soret MCD of Fe(TPP) in excess pyrazine exhibits a slightly distorted S-shaped curve (Table I). The cofacial porphyrin complexes, Fe_2(FTFDU), Fe_2(*m*-FTF6-3,2-NH), and Fe_2(*β*-FTF4-2,1-NH), all give asymmetric S-shaped Soret MCD curves in the presence of pyrazine or of pyrazine and an imidazole-type axial base [both instances are shown for Fe_2(FTFDU) (Figure 14)] that are similar to the Fe(TPP) case (Figures 14, 19, and 21, respectively). This suggests that even with the very restricted cavity of Fe_2(*β*-FTF4-2,1-NH), the second binding site of pyrazine shifts the binding equilibria in favor of the doubly six-coordinate complex.

When carbon monoxide is admitted into solutions of each of the cofacial, diiron porphyrin complexes in the presence of im-

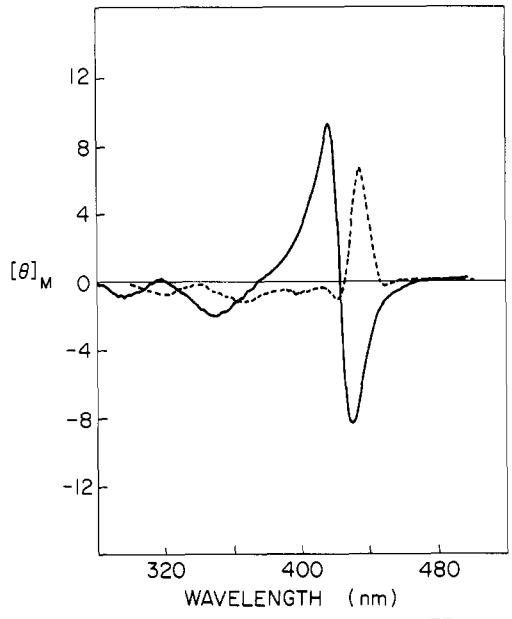

Figure 16. MCD spectra in Soret region of Fe_2(*m*-FTF6-3,2-NH) in 0.01 M 1-TrIm + CO (1 atm) —; in 0.01 M 1-TrIm ---.

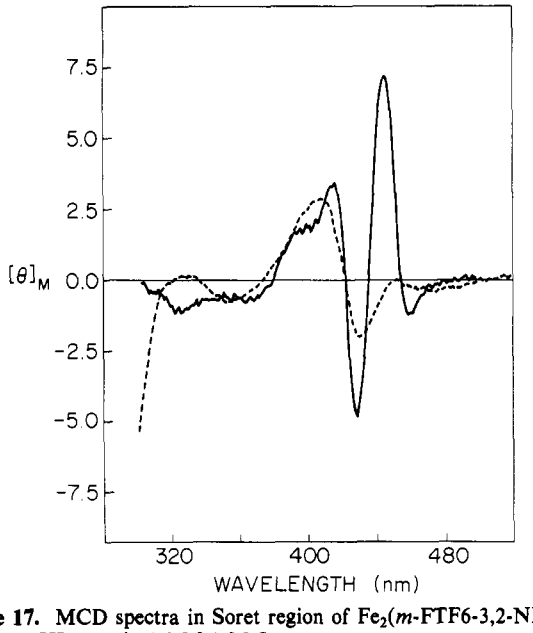

Figure 17. MCD spectra in Soret region of Fe_2(*m*-FTF6-3,2-NH) in 0.03 M 1-HIm —; in 1.0 M 1-MeIm ---.

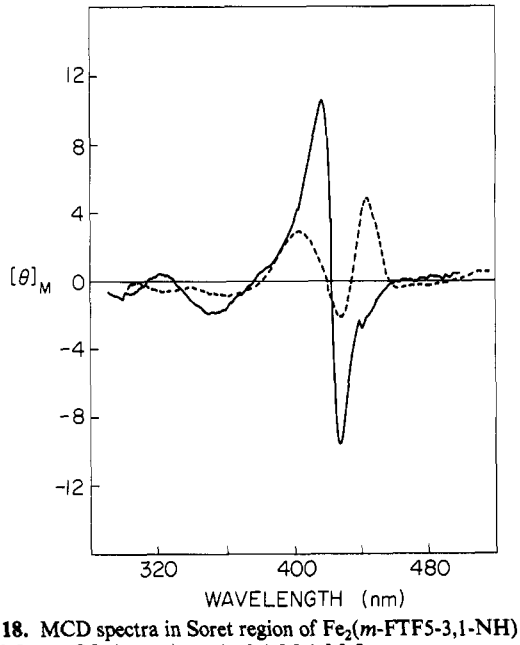

Figure 18. MCD spectra in Soret region of Fe_2(*m*-FTF5-3,1-NH) in 0.1 M 1-MeIm + CO (1 atm) —; in 0.1 M 1-MeIm ---.

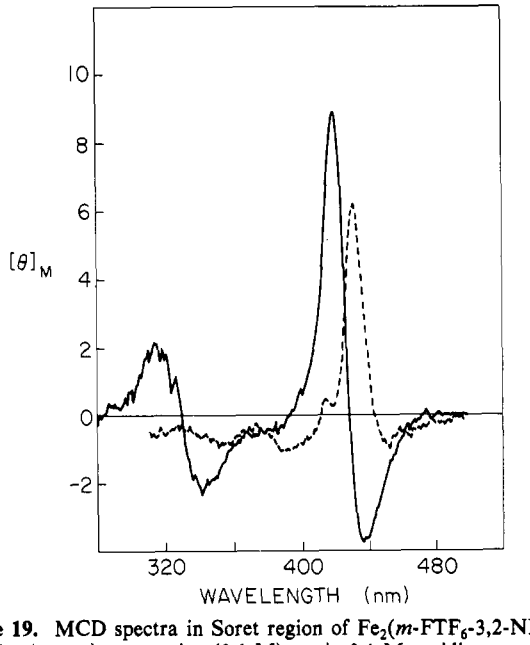

Figure 19. MCD spectra in Soret region of Fe_2(*m*-FTF_6-3,2-NH) in 1-MeIm (excess) + pyrazine (0.1 M) —; in 0.1 M pyridine ---.

idazole axial ligands, MCD suggests that the two metal centers of each molecule become six-coordinate (Figures 14, 16, and 18). It is likely that the carbonyl ligands attach to the internal binding sites, leaving the more bulky nitrogen donors to coordinate externally. The one apparent exception to this behavior is Fe_2-(FTF4-2,1-NH), which shows an extra band on the red side of the main Soret band (Figure 20). This band could be due to incompletely carbonylated porphyrin; i.e., the cavity size is insufficient to allow for the facile coordination of two carbonyl ligands. The extraneous band is in the correct region for a five-coordinate complex. Its reduced intensity can be explained as due to overlap with the adjacent, shorter wavelength, negative MCD band.

Throughout the series of cofacial porphyrin MCD spectra, there are clear differences in band intensities as compared with the model monomers. For instance, for Fe(ADE) it can be seen (Figure 15) that the magnitude of the high-spin band for the 2-methylimidazole adduct is much larger than the positive lobe of the *A*-term of the 1-methylimidazole–carbonyl complex, whereas in the cofacial porphyrin Fe_2(*m*-FTF6-3,2-NH) the band of the high-spin complex is the weaker of the two (Figure 16). Furthermore, the magnitude of the high-spin band of the dimer is approximately one-tenth that of the monomer, while that of the low-spin, carbonyl complex of the binary complex is about one-third that of the monomer. This situation is different from the Fe(TPP) and meso-aryl-linked, cofacial porphyrin case, where the bands for the high-spin complexes are more intense than those of the low-spin, carbonyl–imidazole complexes (Figures 3 and 14). It should be recalled that we have plotted all cofacial porphyrin spectra on a per heme basis. Thus, any disparity between the magnitudes or positions of the bands of the dimers and the monomers indicates either the effects of electronic interaction in the binary porphyrin or distortion in the geometries of the "face-to-face" porphyrins which are different from those in the monomers. Weighing errors probably play a small part in the differences in band magnitudes.

In the early phases of this work, we synthesized the mixed-metal "face-to-face" porphyrin, Fe_ANi_N(*m*-FTF6-3,2-NMe) and the model nickel monomer Ni(ADE), with the intention of examining the coordination at the iron in the cofacial complex, at least qualitatively, by subtracting the spectrum of the nickel monomer

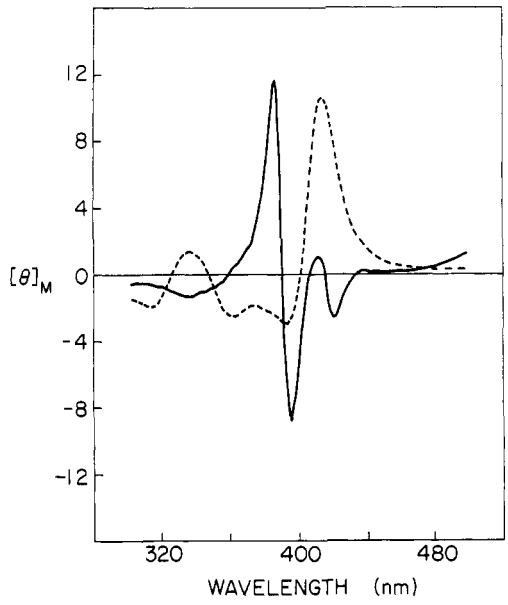

Figure 20. MCD spectra in Soret region of Fe_2(β-FTF4-2,1-NH) in 0.02 M 1-MeIm + CO (1 atm) —; in 0.02 M 1-MeIm ---.

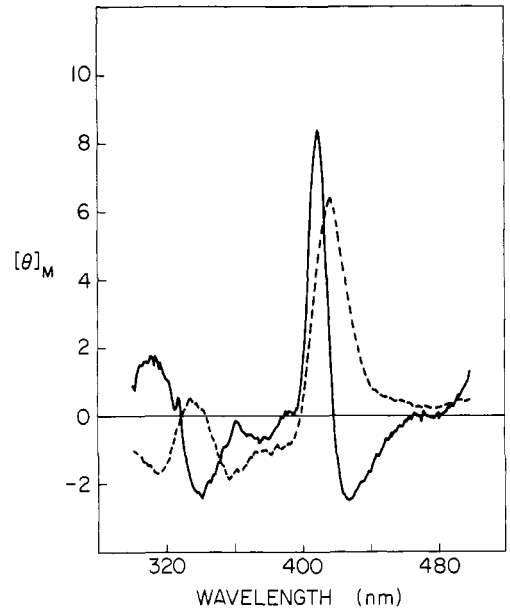

Figure 21. MCD spectra in Soret region of Fe_2(β-FTF4-2,1-NH) in 0.02 M 1-MeIm + 0.01 M pyrazine —; in 0.03 M 1-HIm ---.

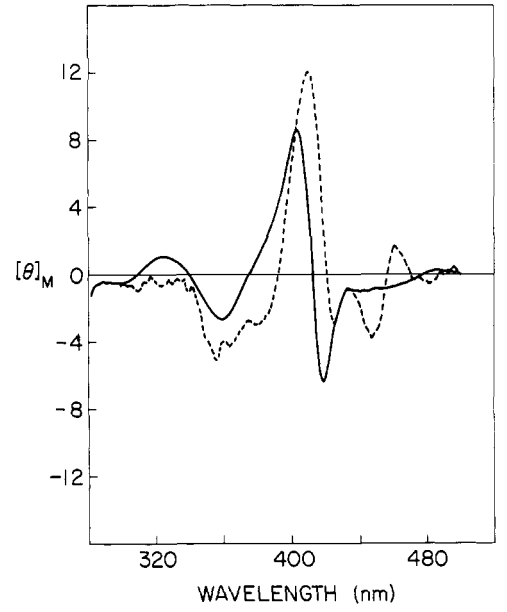

Figure 22. MCD spectra in Soret region of Ni(ADE) —; Fe_ANi_N(β-FTF6-3,2-NM3) ---.

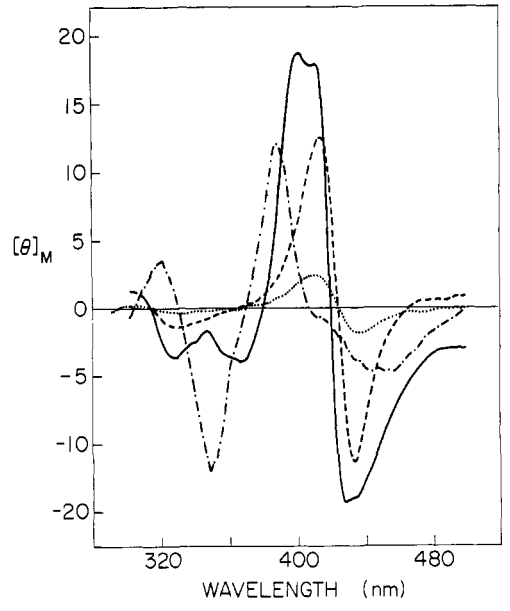

Figure 23. MCD spectra in Soret region of $[Fe(TPP)]_2O$ —; Fe[Piv_3-(4ClmP)P] + O_2 (1 atm) ---; Fe_2(β-FTF4-2,1-NH) in 0.4 M 1-MeIm + O_2 (1 atm) ·····; Fe(PocPivP) in 1-MeIm excess + O_2 (1 atm) · · ·.

from the spectrum of the dimer. Unfortunately, the MCD spectrum of Fe_ANi_N(*m*-FTF6-3,2-NMe) is dominated by the nickel-containing component (Figure 22) and is insensitive to changes in coordination arising from the addition of nitrogenous bases. We have, hence, not pursued this work further.

MCD Determination of the Result of Interaction of Ferrous Porphyrin Complexes with Dioxygen. The interaction of oxygen with iron(II) porphyrins can be followed by MCD. Oxygen can interact with sterically protected heme complexes to form oxygen complexes under ambient conditions. Oxyhemoglobin and oxymyoglobin serve as examples, and the S-shaped, *A*-term Soret MCD band of the latter is shown in Figure 2. Stable, six-coordinate, oxygen adducts are also formed with suitably protected[3] synthetic ferrous porphyrins. The Soret MCD spectrum of one of these, Fe[Piv_3(4ClmP)P](O_2),[13] is shown in Figure 23. A further mode of interaction of hemes with dioxygen is oxidation to give ferric, μ-oxo, dinuclear products. The Soret MCD recorded for $[Fe(TPP)]_2O$ (Figure 23) is a broad S-shaped curve that is distinguishable from the sharper bands of the dioxygen complexes. Thus, the product of the interaction between oxygen and Fe(PocPivP) in the presence of 1-methylimidazole[18] is clearly revealed by its Soret MCD spectrum to be a dioxygen complex and not the μ-oxo, dinuclear species. Again, the magnitudes of the MCD bands of Fe(PocPivP) are lower than those of the noncapped porphyrin (vide supra). Figure 23 also shows the Soret MCD spectrum obtained when dioxygen is admitted to a solution of Fe_2(β-FTF4-2,1-NH) in the presence of 0.4 M 1-methylimidazole. This spectrum is not akin to either of the two alternatives discussed. The nature of this and products similarly derived from the interaction of other cofacial metalloporphyrins with dioxygen are the subject of active research in the Stanford laboratories.

Acknowledgment. We wish to thank Professor Carl Djerassi for his continuing interest in the project; Susana Bencosme for a sample of H_4FTF4-2,1-NH; Mrs. Ruth Records for her care and diligence in measuring the MCD and absorption spectra; Dr. Günter Barth for his data acquisitions programs; and Professor Jack Baldwin for advice on the syntheses of the capped porphyrins. This work was supported by grants from the National Science Foundation (Grant Nos. CHE80-09240, CHE78-09443, and CHE77-22722) and the National Institutes of Health (Grant Nos. HL16833, HL13412, GM20276, and GM17880).