Magnetic Circular Dichroism Study of Porphyrin π Cation Radical Species

WILLIAM R. BROWETT and MARTIN J. STILLMAN*

Department of Chemistry, University of Western Ontario, London, Ont. N6A 5B7, Canada

Received September 8, 1980

Absorption and magnetic circular dichroism (MCD) spectra of selected metalloporphyrins and their bromine oxidized derivatives with bromide or perchlorate counter ions have been measured. The resultant data clearly discriminate between metal and porphyrin π ring oxidation. Further, the MCD spectrum is sensitive to the orbital ordering in the ground state of the π cation radical species formed from ZnTPP, CuOEP and CoOEP. The [ZnTPP]$^{+\cdot}$Br$^-$, [ZnTPP]$^{+\cdot}$ClO$_4^-$, [CuOEP]$^{+\cdot}$ClO$_4^-$, and [Co(III)-OEP]$^{2+\cdot}$2ClO$_4^-$ species each of which has been assigned a $^2A_{2u}$ ground state, exhibit well-defined Faraday A terms under the B (Soret) band in the 400 nm region. In contrast, the data observed for [Co(III)-OEP]$^{2+\cdot}$2Br$^-$, a $^2A_{1u}$ ground state species, does not have the A term character associated with the B band. Both classes of oxidized porphyrins exhibit an apparently characteristic series of weak, overlapping bands between 500 nm and 700 nm in the absorption and MCD spectra. The data show that this region of the MCD spectrum provides an assignment criterion for porphyrin π cation radical species.

Introduction

Much of the interest in porphyrin chemistry and spectroscopy stems from the use of these systems as models for the wide range of biologically active molecules that incorporate a porphyrin or porphyrin-like moiety. Specifically, it seems likely that our understanding of the mechanism for the chemistry of these biological molecules will only be complete when good *in vitro* models have been made.

A porphyrin π cation radical species has been proposed as the electronic configuration of the iron porphyrin group in the horseradish peroxidase and catalase peroxide reaction intermediates, the compound I species [1–7]. Similar π cation radical species are also implicated in the chlorophyll photochemical reaction for the primary products generated by the photooxidation of the chlorins in photosystems I and II [8] and, possibly, in the intermediate in the cytochrome P$_{450}$ reaction sequence [9]. Characterization of the electronic configuration of the porphyrin π cation radical species that are considered models of these protein intermediates is based primarily on EPR assignments [5].

Magnetic circular dichroism (MCD) spectroscopy has been used with considerable success to unravel complex porphyrin and phthalocyanine spectra because it provides direct information about the angular momentum distribution in each of the excited states in these highly symmetric species [10–14]. These additional assignment and 'fingerprinting' properties allow the absorption spectrum to be used to its fullest extent for characterization of the electronic configuration of the porphyrin π system in heme proteins.

Oxidation of porphyrin π rings to give π cation radical species dramatically alters the absorption spectrum [1–5]. The reasonably well-resolved bands in the visible (the α and β bands) and UV (the Soret band) regions of the unoxidized porphyrin are replaced by a continuous envelope of absorption that arises from a series of overlapping bands that extend from about 650 nm to beyond 300 nm, with a maximum absorbance in the Soret region at about 410 nm. Identification of individual transitions in these absorption spectra is difficult. MCD spectra provide additional assignment criteria by way of the sign, magnitude and band shape (*i.e.* A, B or C terms) of the signal observed under each absorption band. Thus measurement of MCD spectra for these porphyrin π cation radicals provides a starting point for theoretical analysis of the electronic configuration in these species. Recently, the spectra of several oxidized porphyrin species have been reported [15, 16], however, because these absorption spectra are so poorly resolved and the species are EPR silent, it is difficult to determine whether the species are indeed π cation radicals of the same class that have been previously well characterized [1–5, 17].

---

*Author to whom correspondence should be addressed. Member of the Centre for Chemical Physics, University of Western Ontario.
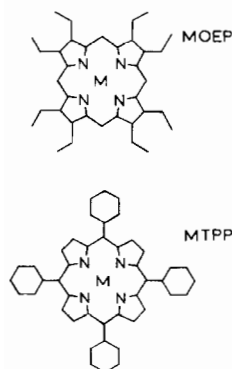
Fig. 1. Molecular geometry of (octaethylporphyrinato)metal-(II) and ($\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinato)metal(II).

In this paper we report the first magnetic circular dichroism spectra of a series of porphyrin π cation radical complexes. These spectra show that there are specific differences between the spectra of oxidized porphyrins with $^2A_{2u}$ and $^2A_{1u}$ ground states. The MCD spectra of these complexes are quite unique and appear to provide a means of identifying porphyrin π cation radical species.

Experimental

The zinc tetraphenylporphyrin and the copper and cobalt octaethylporphyrins were prepared by the acetate method of metal insertion into H_2TPP and H_2OEP*, respectively [18]. The resulting ZnTPP was dried, then redissolved in CH_2Cl_2 and chromatographed on silica gel with benzene. All three metalloporphyrins were recrystallized from CH_2Cl_2 and CH_3OH followed by final drying at 10^{-5} torr to remove the solvent and the volatile impurities. Fig. 1 shows the molecular geometry of these two porphyrin ring systems.

The metalloporphyrins were dissolved in CH_2Cl_2, then oxidized by titration with excess dilute Br_2 in CCl_4 until no further significant spectroscopic change was observed. The bromide to perchlorate ligand exchange was achieved by passing the solution over hydrated $AgClO_4$ obtained from Alfa Inorganics Inc. All solvents were certified A.C.S. spectroanalyzed, and the $Br_2(l)$ was A.C.S. reagent grade, obtained from Fisher Chemicals Inc. Absorption spectra were obtained with a CARY 14 spectrophotometer, using 1 mm and 10 mm cells to record the near ultraviolet and visible region spectra, respectively, at room temperature. The MCD spectra of all the solutions, also at room temperature, were obtained in 10 mm cells using a JASCO J5 spectrometer

*MTPP, ($\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinato)metal(II) and MOEP, (octaethylporphyrinato)metal(II).

with a Sproul SS-20 modification, and a field of 5.5 T from an Oxford Instruments SM2 magnet. The wavelength of the JASCO spectrometer was calibrated to the CARY 14 using holmium (III) and neodymium (III) filters. The CD spectrometer sensitivity was calibrated using recrystallized (+)-d-10-camphor sulfonic acid (Eastman) with a value of $[\theta]_{291}/\epsilon_{285} = 226$ [19]. The field strength and sign were calibrated by measuring the 510 nm MCD spectrum of aqueous $CoSO_4$, $[\theta]_M$ for our instrument was calculated to be -59.3 deg cm^2 dmol^{-1} T^{-1}. The absorption spectra are reported in units of L mol^{-1} cm^{-1} and the MCD spectra are reported in units of deg cm^2 dmol^{-1} T^{-1} [20]. Extinction coefficients of 5.60×10^5 for ZnTPP [1], 3.05×10^5 for CuOEP [21] and 2.29×10^5 for CoOEP [21] for the B band transitions were used to calculate the concentrations. All spectra shown were automatically digitized using a digital sampling unit attached to either the JASCO or CARY 14 wavelength drive and slidewire [22]. Digitized copies of each spectrum were generated on paper tape during the measurement. The baselines were subtracted by computer from the original data. The data presented here are retraced computer plots.

Results

The intense electronic absorption spectra of metalloporphyrins such as MTPP and MOEP arise from singlet $\pi \to \pi^*$ transitions of the D_{4h} 18π electron ring [23, 24]. The Q (or α and β) bands in the visible region of the absorption spectrum are formally forbidden but derive intensity from the strongly allowed B (or Soret) band in the near ultraviolet region through configuration interaction [23]. To higher energy are less intense $\pi \to \pi^*$ transitions labeled the N, L, and M bands [25]. In terms of Gouterman's four-orbital model [23] the B and Q bands are assigned as a_{1u} and $a_{2u} \to e_g$ transitions respectively. The MCD spectrum of a symmetric, diamagnetic porphyrin is typically characterized by two intense, narrow, positive A terms that lie at the Q and B band wavelengths and arise from the magnetically induced splitting of the first two E_u excited states [10, 26]. The magnetic moments in these two bands calculated from MCD data of porphyrins [10, 26, 27] and phthalocyanines [28] agree quite closely with theoretical values [10, 12]. While the simple free electron model predicts values of 1 BM for the Soret band and 9 BM for the Q band [29], two, more recent molecular orbital calculations [10, 12] give magnitudes of the order 4 BM for the Q band, and close to 0.1 BM for the Soret band. Oxidation of the ring to form a π cation radical (Figs. 2 and 3) clearly quenches much of the angular
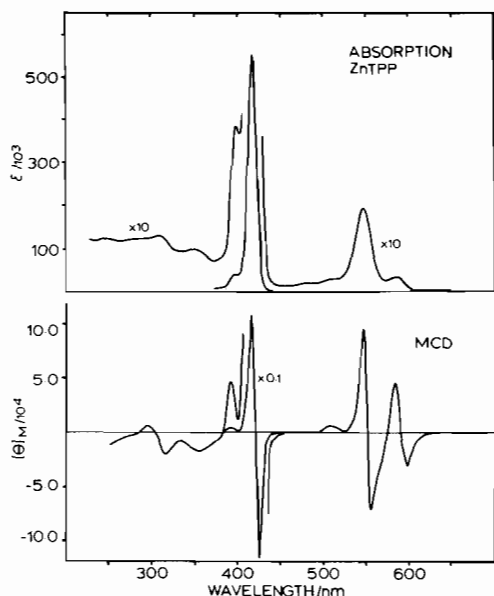
Fig. 2. Absorption and MCD spectra of (α,β,γ,δ-tetraphenyl-porphyrinato)zinc(II) in CH_2Cl_2.

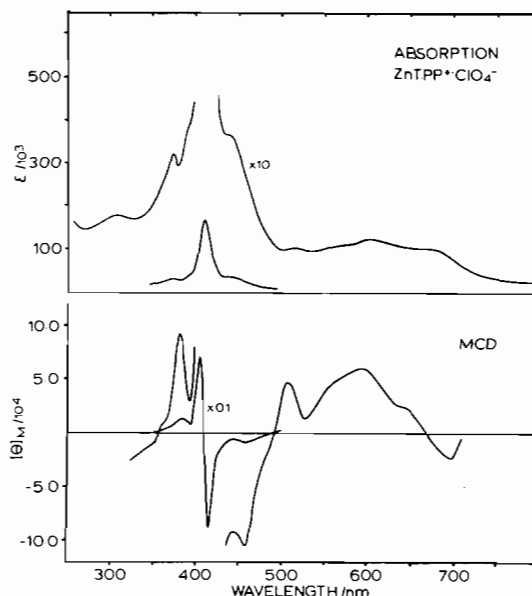Fig. 4. Absorption and MCD spectra of $[ZnTPP]^{+\cdot}ClO_4^-$, perchloro(α,β,γ,δ-tetraphenylporphyrinato)zinc(II) in CH_2-Cl_2.
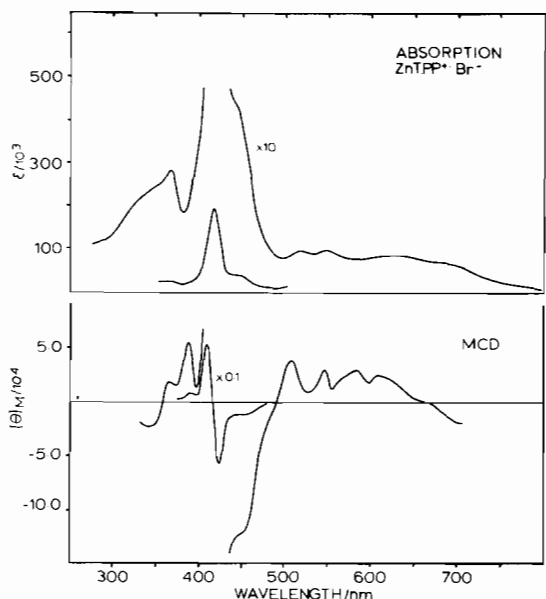
Fig. 3. Absorption and MCD spectra of $[ZnTPP]^{+\cdot}Br^-$, bromo(α,β,γ,δ-tetraphenylporphyrinato)zinc(II) in CH_2Cl_2.

momentum that is evident in the Q bands of unoxidized ring species.

Figures 2–4 show the absorption and MCD spectra of ZnTPP, $[ZnTPP]^{+\cdot}ClO_4^-$ and $[ZnTPP]^{+\cdot}Br^-$ dissolved in dichloromethane. The absorption spectrum of ZnTPP is characterized by a weak Q_{oo} band at 586 nm, with a stronger Q_{vib} band at 547 nm. To higher energy at 419 nm lies the intense B

band. Notably, the MCD spectrum associated with each of these transitions is the derivative-shaped A term characteristic of the degenerate D_{4h} porphyrin transitions of unoxidized species [27]. The slight asymmetry of the envelopes associated with these bands is indicative of T term contributions.

The absorption spectra of both the oxidized ZnTPP species are very similar to that of $[ZnTPP]^{+\cdot}$-ClO_4^- prepared by electrochemical oxidation in the presence of ClO_4^- in CH_2Cl_2 [1]. There are a series of broad, weak transitions between 480 nm and 750 nm for the $[ZnTPP]^{+\cdot}ClO_4^-$ and $[ZnTPP]^{+\cdot}Br^-$ species. In addition, in both species, the B band intensity is reduced relative to the ZnTPP spectrum. The MCD spectra reflect these changes since there is a broad, negative band between 670 nm and 710 nm, while to higher energy, between 490 nm and 670 nm, there are a series of overlapping positive bands. The B band transition in both oxidized species still exhibits A term character, but it is much reduced in intensity when compared with the parent ZnTPP spectrum, Fig. 2. The absorption band at 450 nm in the spectra of the oxidized species which appears as a negative transition in the MCD spectrum is probably a degradation product of ZnTPP, and its concentration increases with subsequent addition of excess Br_2. This degradation may be the result of dication production, $[ZnTPP]^{2+}$, which can act as a strong electrophile, reacting with impurities or the bromide in the sample [4]. Furthermore, despite the addition of a large excess of Br_2, there is approximately a 10% impurity of ZnTPP in the $[ZnTPP]^{+\cdot}$-Br^- sample as indicated by the intensity associated
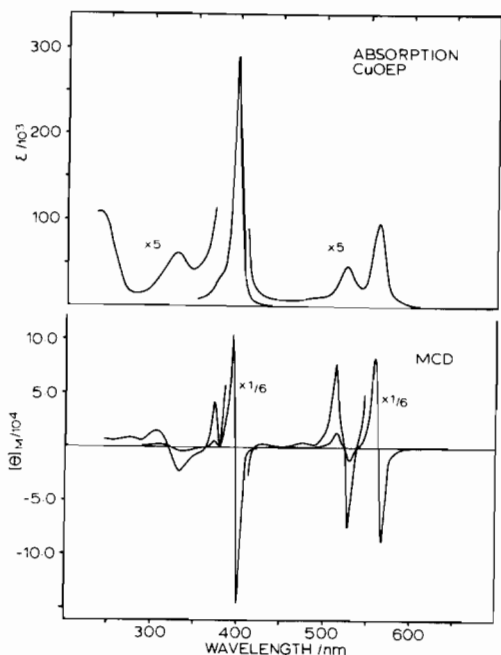
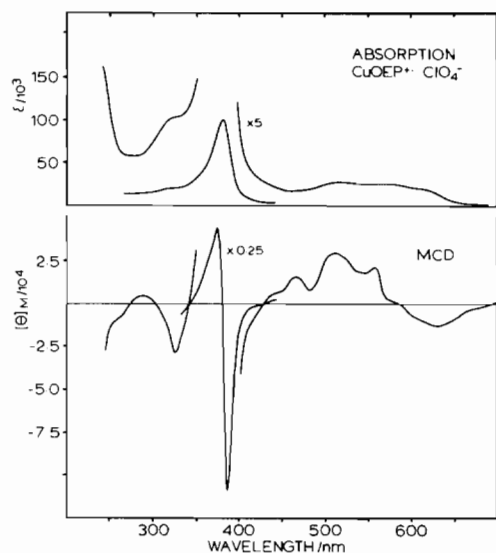Fig. 5. Absorption and MCD spectra of CuOEP (octaethyl-porphyrinato)copper(II) in CH_2Cl_2.

Fig. 6. Absorption and MCD spectra of, $[CuOEP]^{+\cdot}ClO_4^-$, perchloro(octaethylporphyrinato)copper(II) in CH_2Cl_2.

Fig. 7. Absorption and MCD spectra of, CoOEP, (octaethyl-porphyrinato)cobalt(II) in CH_2Cl_2.

with the Q_{vib} transition of ZnTPP at 550 nm. How-ever, when Br^- is replaced by ClO_4^-, only $[ZnTPP]^{+\cdot}$ ClO_4^- appears to be present in solution.

The absorption and MCD spectra of CuOEP and $[CuOEP]^{+\cdot}ClO_4^-$ in CH_2Cl_2 are shown in Figs. 5 and 6. The absorption spectrum of CuOEP in dichloro-methane is characterized by a strong Q_{oo} band at 541 nm, a weak Q_{vib} band at 524 nm and an intense B band at 397 nm. As in the MCD spectrum of
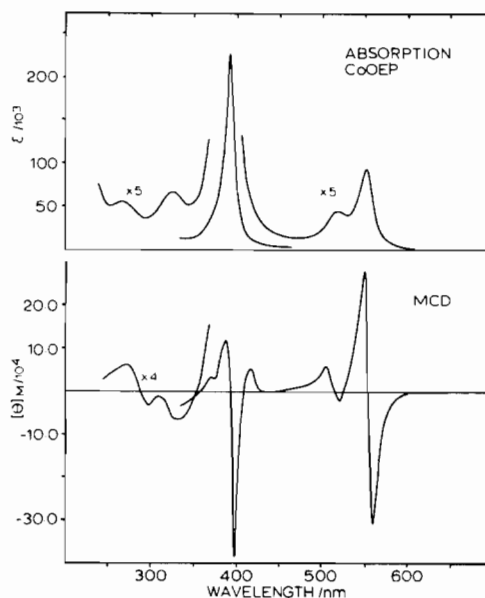
ZnTPP, highly resolved, intense A terms are asso-ciated with the Q_{oo} and B band transitions. However, unlike ZnTPP, the Q_{vib} envelope apparently consists of a series of oppositely signed B terms.

Complete oxidation using bromine, by the addi-tion of excess Br_2 to CuOEP in CH_2Cl_2, was not achieved. The large excess of Br_2 required to oxidize even 50% of the porphyrin resulted in some irrever-sible degradation. However, by using a slight excess of Br_2, followed immediately by ligand exchange to ClO_4^-, complete formation of an oxidized species with an identical absorption spectrum to that of $[CuOEP]^{+\cdot}ClO_4^-$ obtained by ferric perchlorate oxida-tion was achieved [30]. The absorption spectrum of $[CuOEP]^{+\cdot}ClO_4^-$ in CH_2Cl_2 is characterized by a series of broad, indistinct bands between 450 nm and 650 nm, and a much weaker B band at 382 nm. The MCD of $[CuOEP]^{+\cdot}ClO_4^-$ reflects the poorly resolved nature of the visible region absorption spectrum: between 590 nm and 650 nm there is a broad negative band, while to higher energy, between 430 nm and 590 nm there is the familiar series of overlapping positive bands seen initially in the oxidized ZnTPP spectra. As before, the B band appears to have weak A term character. The weak A term at 560 nm indicates the presence of about 0.5% unoxidized CuOEP.

Figures 7 to 11 show the absorption and MCD spectra of CoOEP and a series of oxidized products, with ClO_4^- and Br^- as counter ions. The absorption spectrum of Co(III)OEP, Fig. 7, is characterized by a strong Q_{oo} band at 551 nm, a weak Q_{vib} band at 516 nm, and a B band at 392 nm. There appear to be MCD A terms associated with each of these
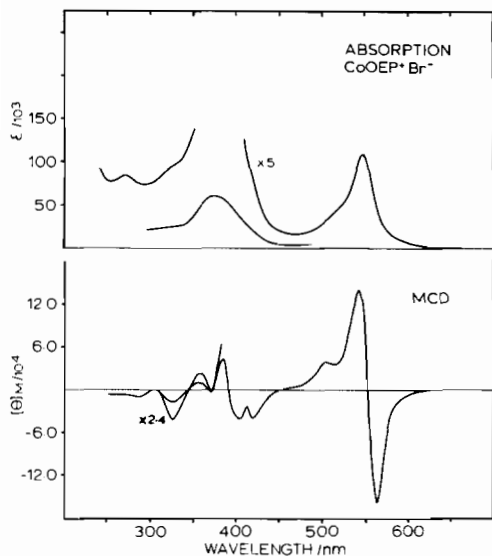
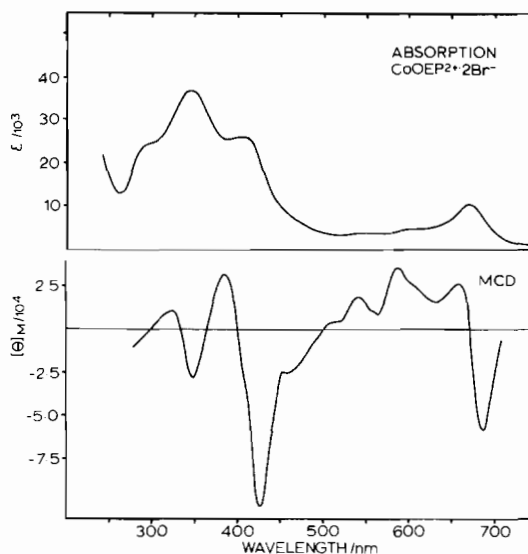Fig. 8. Absorption and MCD spectra of, $[Co(III)OEP]^+Br^-$, bromo(octaethylporphyrinato)cobalt(III) in CH_2Cl_2.

Fig. 10. Absorption and MCD spectra of, $[Co(III)OEP]^{2+\bullet}$ $2Br^-$, dibromo(octaethylporphyrinato)cobalt(III) in CH_2Cl_2.
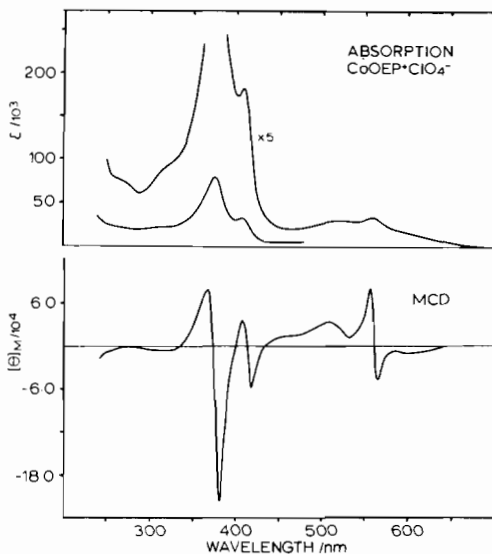

Fig. 9. Absorption and MCD spectra of, $[Co(III)OEP]^+$-ClO_4^-, perchloro(octaethylporphyrinato)cobalt(III) in CH_2-Cl_2.
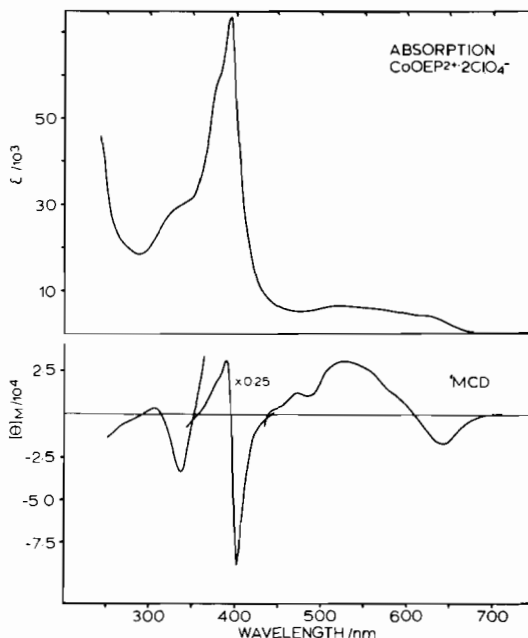

Fig. 11. Absorption and MCD spetra of, $[Co(III)OEP]^{2+\bullet}$ ClO_4^-, diperchloro(octaethylporphyrinato)cobalt(III) in CH_2-Cl_2.

bands, together with positive and negative B terms under the Q_{vib} and B bands, respectively.

There are distinct changes in the absorption spectra when the CoOEP is oxidized to $[Co(III)OEP]^+Br^-$ with Br_2. The Q_{oo} band shifts to 547 nm with a slight increase in intensity, while the Q_{vib} band envelope almost disappears and the B band loses much of its intensity and shifts to 372 nm. Although the Q_{oo} MCD band has been reduced in intensity by a factor of 2, the B band MCD signal is 10 times smaller relative to the unoxidized CoOEP spectrum.

Exchange of Br^- with ClO_4^- results in a significant loss of intensity associated with the Q_{oo} absorption band. To higher energy the B envelope splits into two distinct bands, one at 419 nm and the other, with greater intensity, is at 387 nm. The MCD spectrum appears to be characterized by an A term in the Q_{oo} band region, and two A terms in the B brand region, Fig. 9.

Further oxidation of [Co(III)OEP]$^+$Br$^-$ by Br$_2$ results in the formation of [Co(III)OEP]$^{2+\cdot}$2Br$^-$. This species has an absorption spectrum, Fig. 10, characterized by a distinct band at 670 nm followed by an overlapping series of weaker bands throughout the visible region, while in the B band region there is one weak band at 410 nm, the most intense band is centered at 344 nm. The MCD spectrum in the visible region of this species is dominated by an apparent A term centered on 670 nm, followed by a series of positive bands between 500 nm and 630 nm. In the B band region of the spectrum, there is what appears to be a distorted A term, however, it is not centered under a clearly defined absorption band. The weak A term at 550 nm is probably due to a 4% impurity of [Co(III)OEP]$^+$Br$^-$.

[Co(III)OEP]$^{2+\cdot}$2ClO$_4^-$ is formed by exchange of Br$^-$ with ClO$_4^-$ from the [Co(III)OEP]$^{2+\cdot}$2Br$^-$ complex. The absorption and MCD spectra, Fig. 11, closely resemble that of [CuOEP]$^{+\cdot}$ClO$_4^-$, in particular, the MCD is characterized by an A term under the B band, and the familiar envelope of bands spread throughout the visible region.

Discussion

Metal complexation of the tetradentate porphyrin ligand must take into account the various sizes and chelation abilities of different porphyrin dianions (*e.g.*, OEP, TPP, OMBP and Pc). Though the metal-nitrogen bond lengths are not fixed within each porphyrin, the core size of the porphyrin ligand is limited in terms of its expansion and contraction, resulting in doming of oversized metal cations [31]. The Zn(II) cation appears to be borderline in its ability to remain coordinated in the centre of the porphyrin ligand. It does however, appear to exhibit D$_{4h}$ symmetry in CH$_2$Cl$_2$. The toluene solvate ZnTPP crystal X-ray data clearly indicates that ZnTPP is four coordinate with the metal lying in the plane of the ligand and having compressed Zn to nitrogen bonds [32]. When fully dissolved in toluene, the complex is expected to remain four coordinate, and, indeed, its absorption spectrum is very similar to that of ZnTPP dissolved in CH$_2$Cl$_2$ [33]. The B band is at 419 nm, and the intensity ratio of the Q$_{oo}$ to Q$_{vib}$ bands is low. ZnTPP will readily form a five-coordinate complex with most solvents or anionic ligands which results in a red shift of the B band and an increase in the intensity ratio of the Q bands [33].

The absorption and MCD spectra shown in Fig. 2 are qualitatively similar to ZnTPP dissolved in polymethylmethacrylate in which A terms are clearly associated with the Q$_{oo}$, Q$_{vib}$ and B bands [14]. The Q bands of the zinc(II) porphyrin in EPA have been studied in considerable detail using high resolution Zeeman and MCD spectra [13]. Analysis indicated that the angular momentum associated with the Q$_{oo}$ band was significantly reduced to Jahn–Teller coupling. In addition, the Q$_{vib}$ MCD band was partially resolved into its individual vibronic components at low temperatures, which consisted of B terms together with positive and negative A terms, the signs of which depended upon whether the symmetry of the transition to the vibrational level is *a* or *b*, respectively.

The absorption and MCD spectra of the oxidized ZnTPP, Figs. 3 and 4, indicate that there has been a significant change in the number and type of transitions associated with the Q band region, the a$_{2u} \rightarrow$ e$_g$ transition. The resolved A terms of the unoxidized ZnTPP, Fig. 2, have been replaced by B terms. However, in the B band region, the a$_{1u} \rightarrow$ e$_g$ transition, the A term in the ZnTPP MCD spectrum has been retained, though with much less intensity when compared with the spectrum of the unoxidized species. The oxidized [ZnTPP]$^{+\cdot}$X$^-$ species is expected to be five coordinate, with both ClO$_4^-$ and Br$^-$ counter ions, despite the fact that ClO$_4^-$ is considered to be noncoordinating, since the crystal structure of [ZnTPP]ClO$_4$ appears to be indistinguishable from other five coordinate ZnTPP complexes [34]. The five coordination in the solid appears to persist in solution as the perchlorate asymmetric-stretching band in the IR is split [34]. The change in coordination when the ZnTPP is complexed with anionic halides or neutral ligands, from four coordinate in noncoordinating solvents, to five coordinate in more polar solvents, has been associated with a red shift of the B band and correlated with the charge and polarization of the axial ligands and their resulting ability to transfer charge to the poprhyrin ring *via* the Zn atom [32]. Comparison of the [ZnTPP]$^{+\cdot}$X$^-$ spectra of perchlorate and bromide also indicate a similar trend despite the weak metal-to-porphyrin π cation radical interaction indicated in the EPR spectrum [35].

The ^{2}B$_{2g}$ CuOEP absorption and MCD spectra obtained in CH$_2$Cl$_2$ at room temperature, Fig, 4, are very similar to spectra obtained in polymethylmethacrylate [27]. There is little temperature dependence between 300 K to 8 K indicating that the unpaired electron on the copper does not significantly interact with the porphyrin electronic system. However, lowering the temperature does partly resolve the vibronic components of the Q$_{vib}$ band [27].

[Cu(II)OEP]$^{+\cdot}$ClO$_4^-$, like [Cu(II)TPP]$^{+\cdot}$ClO$_4^-$, has been characterized from the absorption spectrum as a ^{2}A$_{2u}$ ground state species [3, 66]. Since there is an unpaired electron on both the metal and the porphyrin in the oxidized species, spin coupling results in an EPR silent complex. Although monomeric at room temperature, an EPR signal observed at 100 K

has been assigned to a $[CuOEP]^{+\cdot}ClO_4^-$ dimer [37]. Unlike $[MTPP]^{+\cdot}$ species, in which the bulky phenyl groups prevent dimerization, aggregation is common for MOEP and $[MOEP]^{+\cdot}$ species [38]. $ZnOEP^{+\cdot}$ is thought to dimerize by $\pi-\pi$ overlap with coordinating counter ions on either side of the dimer compensating for the positive charge on the oxidized porphyrin [39, 40].

The absorption and MCD spectra of the unoxidized CoOEP in CH_2Cl_2, Fig. 7 are qualitatively similar to previously reported data [27], except that the ratio of the Q to B band intensities in the MCD spectrum reported here is somewhat lower than in the published spectra. However, the spectra of CoOEP in Fig. 7 are similar to spectra of Co dimethylmesoporphyrin IX [41]. The distorted A term associated with the B transition appears to be characteristic of Co porphyrins, for it also occurs in the spectrum of CoTPP in polymethylmetacrylate [14].

The oxidation of Co(II)OEP with bromine in CH_2Cl_2 proceeds in two distinct steps as:

$$Co(II)OEP \xrightarrow{\frac{1}{2}Br_2} [Co(III)OEP]Br \xrightarrow{\frac{1}{2}Br_2}$$

$$[Co(III)OEP]^{2+\cdot}2Br^-$$
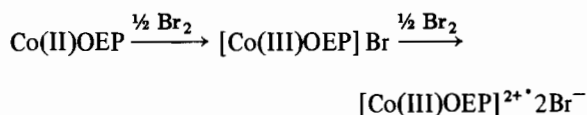
The absorption spectra of $[Co(III)OEP]^+$ with Br^- and ClO_4^- counter ions essentially agree with the previously published data [4] with the exception of the B band region of the $[Co(III)OEP]Br$ spectrum which does not have a distinct transition at 420 nm. The MCD spectra of these Co(III) species appear to be quite unlike other Co(III) diamagnetic porphyrin spectra due to the extremely low intensity in the B band region. For $[Co(III)OEP]Br$ there appear to be A terms associated with each of the distinct bands in the B region of the spectrum. The anomolous nature of these spectra may be indicative of dimerization.

Further oxidation of $[Co(III)OEB]Br$ results in the formation of the π cation radical $[Co(III)OEP]^{2+\cdot}$ $2Br^-$ and, with ligand exchange, $[Co(III)OEP]^{2+\cdot}$ $2ClO_4^-$. The absorption spectra of each of these species agree closely with those previously reported [4] and have been associated with $^2A_{1u}$ and $^2A_{2u}$ ground state π cation radical species, respectively. The absorption spectrum of the $^2A_{1u}$ π cation radical species appears to be characterized by a distinct band at 670 nm which, in the MCD spectrum, can be associated with a distorted A term. This band is now qualitatively similar to the $a_{1u} \rightarrow e_g$ transitions in H_2Pc or Li_2Pc [42]. The low intensity B bands observed for both the absorption and MCD spectra of the $^2A_{1u}$ oxidized porphyrins are similar to the very weak bands found in the B region of many metal phthalocyanine spectra, where the intensity is associated with an $a_{2u} \rightarrow e_g$ transition [43]. The N

band transition, which appears either as a shoulder or as a distinct band in the unoxidized porphyrins, is seen clearly as a negative band near 350 nm in the MCD spectrum of the $^2A_{2u}$ π cation species, Fig. 11. A similar band is also observed in the MCD spectrum of the $^2A_{1u}$ $[Co(III)OEP]^{2+\cdot}2Br^-$ species, indicating that the more intense band at 344 nm in the absorption spectrum is the N band, while the lower energy band at 410 nm should be associated with the B band.

Comparison of $[CuOEP]^{+\cdot}ClO_4$ and $[Co(III)OEP]^{2+\cdot}2ClO_4^-$ spectra indicate that the similarities observed in the absorption spectra of these $^2A_{2u}$ ground state species are strongly reflected in MCD spectra, Figs. 6 and 10. The differing metals, the diamagnetic Co(III) and the paramagnetic Cu(II), appear to affect only the energy of the transitions through a crystal field or electrostatic perturbation of the transition energies. The B band of the $[Co(III)OEP]^{2+\cdot}$ is at 393 nm whereas the $[Cu(II)OEP]^{+\cdot}$ B band is at 382 nm. As with $[ZnTPP]^{+\cdot}$, the MCD spectra of these species indicate that the $a_{2u} \rightarrow e_g$ transition of the B band has been relatively unaffected. Furthermore, the negative B term under the low energy absorption band at about 650 nm in the visible region of the $^2A_{2u}$ π cation radicals appears to be a constant feature.

With the measurement of MCD spectra for a series of porphyrin π cation radicals now available it will be possible to begin an assignment of a typical spectrum in the manner of the analysis for unoxidized porphyrins [23]. At present the only calculations available for π cation radical species do not include angular momentum values or the energies of the excited states, thus it is rather difficult to associate the rather large number of bands observed in these spectra with a particular transition. It is necessary that an MCD spectral line shape be calculated to confirm the accuracy of an assignment.

The final aspect of these data concerns the similarities between the porphyrin π cation spectra and the spectra observed for the compound I species of horseradish peroxidase and catalase [5]. In a series of papers Dolphin and coworkers [1–5] associated the absorption spectra of two cobalt π cation species, one with bromide, Fig. 10, the other with perchlorate, Fig, 11, counterions with the spectra of catalase and horseradish peroxidase compounds I, respectively. The basis for this characterization was the closeness in the alignment of the various sets of absorption spectra. However, the enzyme spectra, and the porphyrin model spectra, actually only match over quite a limited region. MCD data of both enzymes are now available [6, 7] and the correspondence between the model data and the enzyme data can now be put on a firmer footing. The characteristic MCD envelope observed in the visible region, 500–700 nm, of these por-

phyrin π cation radical species is also found in each compound I spectrum. This provides the necessary substansive evidence to support the claim made earlier [5] that the compound I intermediates of these two enzymes contain a π cation radical heme.

Conclusion

The MCD spectrum clearly identifies porphyrin species in which ring oxidation has taken place, rather than the specific oxidation of the central metal cation. Oxidation of the ring to a π cation radical is accompanied by the appearance of a distinctive band envelope in the MCD spectrum that extends throughout the visible region and is characterized by a negative band at about 650 nm, followed by overlapping positive bands to 500 nm. Below 500 nm, the MCD spectrum differentiates between the two classes of π cation radical, those with $^2A_{2u}$ and those with $^2A_{1u}$ ground state configurations. Of the series of porphyrins discussed in this paper, the $[Co(III)OEP]^{2+\cdot}2Br^-$ spectrum is unique in that both the visible and the B band region MCD intensities are markedly reduced when compared with the parent CoOEP spectrum. The B band region MCD A term remains dominant in the spectra of the $^2A_{2u}$ π cation radical species.

Following the analysis of Dolphin and coworkers [4, 5], we identify the electronic configuration of the ground state in the ring oxidized CoOEP in the presence of the bromide ligand as $^2A_{1u}$, in contrast to the $^2A_{2u}$ for each of the other species. Thus, the spectrum of the species with an $^2A_{1u}$ ground state approximates an oxidized phthalocyanine. The absorption and MCD spectra of phthalocyanines (with an a_{1u} highest occupied MO) typically exhibit weak overlapping bands in the Soret region, compared with the intense bands observed for porphyrins (where the orbital ordering is reversed [28, 43]). Those porphyrins in which the a_{2u} is the highest occupied MO for the oxidized species, exhibit a scrambling in the visible region where the band intensity arises from an $a_{2u} \rightarrow e_g$ transition, but maintain an almost normal Soret region from the unaffected $a_{1u} \rightarrow e_g$ transition. This lack of sensitivity may well result from the electron density pattern of the a_{1u} orbital which places nodes on the methine carbon, the pyrrole nitrogens and the central metal [23].

Acknowledgements

References

1 J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc., 92*, 3451 (1970).
2 D. Dolphin, A. Forman, D. C. Borg, J. Fajer, and R. H. Felton, *Proc. Natl. Acad. Sci., 68*, 614–618 (1971).
3 R. H. Felton, G. S. Owen, D. Dolphin, A. Forman, D. C. Borg, and J. Fajer, *Ann. N.Y. Acad. Sci., 206*, 504–515 (1973).
4 D. Dolphin, Z. Muljiani, K. Rousseau, D. C. Borg, J. Fajer, and R. H. Felton, *Ann. N.Y. Acad. Sci., 206* 177–200 (1973).
5 D. Dolphin, and R. H. Felton, *Acc. Chem. Res., 7*, 26–32 (1974).
6 M. J. Stillman, B. R. Hollebone, and J. S. Stillman, *Biochem. Biophys. Res. Comm., 72*, 554–559 (1976).
7 W. R. Browett, and M. J. Stillman, *Biochim. Biophys. Acta, 623*, 21–31 (1980).
8 M. S. Davis, A. Forman, and J. Fajer, *Proc. Natl. Acad. Sci. U.S.A., 76*, 4170–4174 (1979).
9 P. J. O'Brien, *Pharm. Theoret., 42*, 517–536 (1978).
10 A. J. McHugh, M. Gouterman, and C. Weiss, Jr., *Theor. Chim. Acta, 24*, 346–370 (1973).
11 J. C. Sutherland, *The Porphyrins, 3*, 225–248 (1978).
12 A. Kaito, T. Nozawa, T. Yamamoto, M. Hatano, and Y. Orii, *Chem. Phys. Lett., 52*, 154–160 (1977).
13 E. C. M. Kielman-Van Luijt, H. P. J. M. Dekkers, and G. W. Canters, *Molec. Phys., 32*, 899–919 (1976).
14 H. Kobayashi, *Adv. Biophys., 8*, 191–222 (1975).
15 D. Mansuy, M. Lange, and J. C. Chottard, *J. Am. Chem. Soc., 101*, 6437 (1979).
16 C. K. Chang, and K. Ming-Shang, *J. Am. Chem. Soc., 101*, 3413–3415 (1979).
17 J. Fajer, and M. S. Davis, *The Porphyrins, 4*, 197–256 (1978).
18 J. H. Fuhrhop, and K. M. Smith, 'Porphyrins and Metalloporphyrins', ed. K. M. Smith, Elsevier, Amsterdam, The Netherlands, pp. 757–869 (1975).
19 G. C. Chen, and J. T. Yang, *Anal. Lett., 10*, 1195–1207 (1977).
20 B. Holmquist, and B. L. Vallee, *Methods in Enzymology, 49*, 149–179 (1978).
21 K. M. Smith, ref. 18, pp. 884–886.
22 M. J. Scheiring, and M. J. Stillman, unpublished results.
23 M. Gouterman, *The Porphyrins, 3*, 1–165 (1978).
24 M. Gouterman, *N.Y. Acad. Sci., 206*, 70–83 (1973).
25 L. Edwards, D. Dolphin, and M. Gouterman, *J. Molec. Spectrosc., 35*, 90–109 (1970).
26 A. E. Dratz, *Ph.D. Thesis*, University of California at Berkeley, 1966.
27 R. Gale, A. J. McCaffery, and M. D. Rowe, *J. Chem. Soc. Dalton*, 596–604 (1972).
28 M. J. Stillman, and A. J. Thomson, *J. Chem. Soc. Farad. Trans. II, 70*, 790–804 (1974); *ibid. II, 70*, 805–814 (1974).
29 W. T. Simpson, *J. Chem. Phys., 17*, 1218–1221 (1949).
30 J. H. Fuhrhop and D. Mauzerall, *J. Am. Chem. Soc., 91*, 4174–4181 (1969).
31 W. R. Scheidt, *The Porphyrins 3*, 463–511 (1978).
32 W. R. Scheidt, M. E. Kastner and K. Hatano, *Inorg. Chem., 17*, 706 (1978).
33 M. Nappa, and J. S. Valentine, *J. Am. Chem. Soc., 100*, 5075–5080 (1978).
34 L. D. Spaulding, P. G. Eller, J. A. Bertrand, and R. H. Felton, *J. Am. Chem. Soc., 96*, 982–987 (1974).
35 J. Fajer, P. C. Borg, A. Forman, R. H. Felton, L. Vegh, and D. Dolphin, *N.Y. Acad. Sci., 206*, 349 (1973).
36 A. Wolberg, and J. Manassen, *J. Am. Chem. Soc., 92*, 2982–2991 (1970).
37 C. Mengersen, J. Subramanian, and J. H. Fuhrhop, *Molec. Phys., 32*, 893–897 (1976).

38 K. A. Zachariasse, and P. G. Whitten, *Chem. Phys. Lett.,* *23,* 527–532 (1973).

39 R. H. Felton, *The Porphyrins, 5,* 53–125 (1978).

40 J. H. Fuhrhop, P. Wasser, D. Riesner, and D. Mauzerall, *J. Am. Chem. Soc., 94,* 7996–8001 (1972).

41 T. Nozawa, M. Hatano, H. Yamamoto, and T. Kwan, *Bioinorganic Chem., 6,* 267–273 (1973).

42 K. A. Martin, and M. J. Stillman, *Can. J. Chem., 57,* 1111–1113 (1979).

43 K. A. Martin, *M.Sc. Thesis,* University of Western Ontario, Canada, (1979).