Inorg. Chem. **1988**, *27*, 4619–4622

Contribution from the Department of Chemistry,
The University of Western Ontario, London, Ontario, Canada N6A 5B7

Temperature Dependence in the Magnetic Circular Dichroism Spectrum of the π-Cation-Radical Species of Cobalt Octaethylporphyrin

Zbigniew Gasyna, William R. Browett, and Martin J. Stillman*

Received February 3, 1988

The oxidation of metalloporphyrins can result in the formation of π-cation-radical species for which two ground states are possible, namely the $^2A_{1u}$ and $^2A_{2u}$ states. Two-electron oxidation of cobalt(II) octaethylporphyrin yields the π-cation-radical species $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{X}^-)_2$, which exhibits absorption and MCD spectra, in solution and at room temperature, that depend on the counteranion X^-. Complexation with bromide and perchlorate counterions forms different $[\mathrm{Co^{III}OEP}]^{\bullet 2+}$ species that adopt the $^2A_{1u}$ and $^2A_{2u}$ ground states, respectively. The MCD spectral characteristics of the $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Br}^-)_2$ and $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{ClO_4}^-)_2$ complexes differentiate between the two ground states. The MCD spectra in the visible–UV region of both $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Br}^-)_2$ and $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{ClO_4}^-)_2$ are shown, for the first time, to be temperature dependent between 4.2 and 100 K. The temperature dependence in the MCD spectrum is interpreted in terms of spin–orbit coupling in the excited π–π^* states that results when charge-transfer states that involve the cobalt lie close to the π–π^* states. The spin–orbit coupling coefficient modifies the energies of the initially, equally spaced $L{\cdot}S$ components of the porphyrin ^2E_g excited state. The MCD *C* terms that are measured can be characterized as being spin-dependent *C* terms.

Introduction

Oxidation of D_{4h} metalloporphyrin[1-3] and metallophthalocyanine[4] π ring systems significantly alters the absorption spectra, so that in each the well-defined $\pi \rightarrow \pi^*$ Q band (assigned as $a_{2u} \rightarrow e_g$) and B or Soret band (assigned as $a_{1u} \rightarrow e_g$)[5] are replaced by a complicated spectrum that arises from a series of overlapping bands.[6] The overall shape of this spectral envelope has long served as a discriminating criterion for determining which of the two possible electronic ground states of the π-cation-radical species is present. Whereas the electronic configuration of $a_{1u}(2)$ $a_{2u}(1)$ $e_g(0)$ is found for a "normal" porphyrin π cation radical, for example $\mathrm{ZnTPP}^{\bullet +}$, the less usual configuration of $a_{2u}(2)$ $a_{1u}(1)$ $e_g(0)$ is found for $\mathrm{MgOEP}^{\bullet +}$. The ground states of these two model species are defined as having either $^2A_{2u}$ or $^2A_{1u}$ symmetry,[7,8] respectively. Neither the absorption nor the magnetic circular dichroism (MCD) spectrum has been assigned, partly because of difficulty in finding the degenerate transitions that are expected in the spectra of symmetric porphyrin species.[9-13]

Cobalt(II) octaethylporphyrin, $\mathrm{Co^{II}OEP}$, may be oxidized electrochemically[1] and chemically[2,3] in two, consecutive, one-electron steps to π-cation-radical species $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{X}^-)_2$ (X^- = an axially coordinated counteranion). On the basis of distinctly different optical absorption, MCD, and ESR spectral data,[6-8] it has been proposed that $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Br}^-)_2$ and $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{ClO_4}^-)_2$ adopt the $^2A_{1u}$ and $^2A_{2u}$ ground states, respectively. However, recent studies of these radicals interpreted NMR spectral data in terms of a thermal equilibrium between the $^2A_{1u}$ and $^2A_{2u}$ states, with a greater contribution being made by the $^2A_{1u}$ state for the perchlorate compound;[14] this conclusion contrasts with the previous assignments.[6-8] Direct chemical evidence for the different distribution of the unpaired spin density in the two π-cation-radical complexes has been provided[15] by studies of the reactivity of the porphyrin ring.

In this work, we report on the spectral properties of these two model π-cation-radical species, $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Br}^-)_2$ and $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{ClO_4}^-)_2$, using absorption and MCD spectroscopies at temperatures between 4 and 298 K. We demonstrate that the MCD spectra of both species are temperature dependent, and find, for the first time, an indication of the predicted degeneracy of the excited states. We see no indication of an equilibrium mixture between the two ground states in either complex.

Experimental Section

$\mathrm{Co^{II}OEP}$ was purchased from Aldrich. The metalloporphyrin was dissolved in purified $\mathrm{CH_2Cl_2}$ (BDH Chemicals). $\mathrm{Co^{II}OEP}$ was oxidized at room temperature to $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Br}^-)_2$ by using $\mathrm{Br_2}$ dissolved in $\mathrm{CCl_4}$. This gave a product similar to that obtained by photooxidation of $\mathrm{Co^{II}OEP}$ to $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Cl}^-)_2$ carried out in $\mathrm{CH_2Cl_2}$ solution that contained 20% (v/v) $\mathrm{CCl_4}$.[16,17] $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{ClO_4}^-)_2$ was produced from $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Br}^-)_2$ by a bromide to perchlorate ligand exchange over solid $\mathrm{AgClO_4}$. Aliquots of the oxidized porphyrin species diluted with 2-butyl chloride solvent (1:1 v/v) were rapidly transferred to an aluminum cell, which was plunged into liquid nitrogen to form the glass.

Absorption spectra were obtained with a Cary Model 219 spectrophotometer. MCD spectra were obtained with a JASCO J-500C spectropolarimeter controlled by an IBM Instruments S9001 computer using the computer program CDSCAN5.[18] The magnetic field was provided by an Oxford Instruments SM4 superconducting magnet. The temperature of the sample was monitored by using the Oxford Instruments CLTS temperature sensor. The magnetic field strength and sign were calibrated by using the visible-region band of aqueous $\mathrm{CoSO_4}$, for which a value of $\Delta\epsilon_M = -1.9 \times 10^{-2}\ \mathrm{L\ mol^{-1}\ cm^{-1}\ T^{-1}}$ at 510 nm was calculated. Spectra Manager, a spectral data base program developed in this laboratory for use with the IBM S9001, PC/RT, and PS/2 microcomputers, was used for the spectral data manipulation, analysis, and plotting.[19] The MCD expressions taken from Piepho and Schatz were used.[20]

Results

A number of compounds with a structure analogous to that of $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{X}^-)_2$ can be produced by using various oxidation

---

* To whom correspondence should be addressed.

(1) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 5, p 53.
(2) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982.
(3) Dolphin, D.; Muljiani, Z.; Rousseau, K.; Borg, D. C.; Fajer, J.; Felton, R. H. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 177.
(4) Nyokong, T.; Gasyna, Z.; Stillman, M. J. *Inorg. Chem.* **1987**, *26*, 548.
(5) Gouterman, J. *J. Chem. Phys.* **1959**, *30*, 1139.
(6) Browett, W. R.; Stillman, M. J. *Inorg. Chim. Acta* **1981**, *49*, 69.
(7) Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 349.
(8) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 4, p 197.
(9) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 3, Part A, p 1.
(10) McHugh, A. J.; Gouterman, M.; Weiss, C. *Theor. Chim. Acta* **1972**, *24*, 346.
(11) Edwards, W. D.; Zerner, M. C. *Can. J. Chem.* **1985**, *63*, 1763.
(12) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *ACS Symp. Ser.* **1986**, *No. 321*, 298.
(13) Nyokong, T.; Gasyna, Z.; Stillman, M. J. *Inorg. Chem.* **1987**, *26*, 1087.
(14) Morishima, I.; Takamuki, Y.; Shiro, Y. *J. Am. Chem. Soc.* **1984**, *106*, 7666.
(15) Setsune, J.-I.; Ikeda, M.; Kishimoto, Y.; Kitao, T. *J. Am. Chem. Soc.* **1986**, *108*, 1309.
(16) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1984**, *23*, 382.
(17) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1985**, *24*, 2440.
(18) Gasyna, Z.; Browett, W. R.; Nyokong, T.; Kitchenham, R.; Stillman, M. J. *Chemom. Intell. Lab. Syst.*, in press.
(19) Browett, W. R.; Stillman, M. J. *Comput. Chem.* **1987**, *11*, 73.
(20) Piepho, S. B.; Schatz, P. N. *Group Theory in Spectroscopy, with Applications to Magnetic Circular Dichroism*; Wiley: New York, 1983.
(21) Gasyna, Z.; Stillman, M. J. Unpublished data.

0020-1669/88/1327-4619$01.50/0

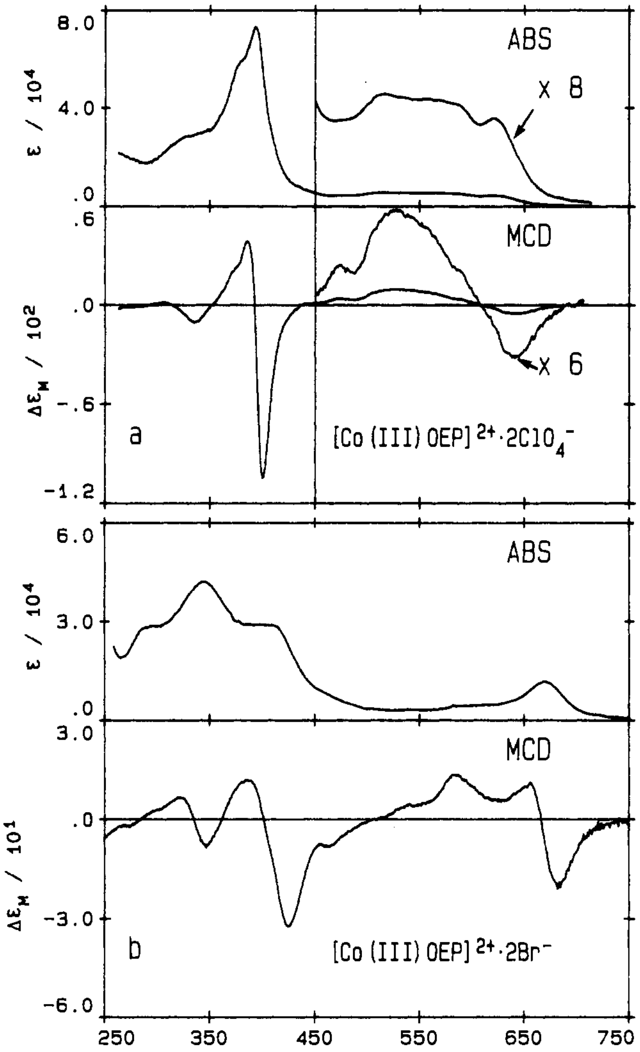

Figure 1. Optical absorption and MCD spectra of (a) the $^2A_{2u}$ radical $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$ and (b) the $^2A_{1u}$ radical $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ recorded in CH_2Cl_2 at 298 K.

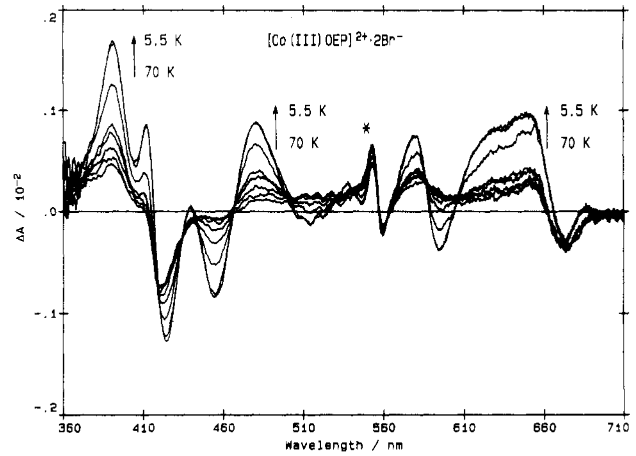

Figure 2. Temperature dependence of the MCD spectrum of $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ in a glassy 2-butyl chloride–CH_2Cl_2 mixture (1:1 v/v). The spectra were taken at 5.5, 7.8, 10, 15, 20, 30, 50, and 70 K, at a magnetic flux density of 2.81 T. The star marks a band due to unreacted $Co^{II}OEP$.

methods. In particular, compounds with $X^- = Cl^-$, Br^-, ClO_4^-, or $SbCl_6^-$ can be obtained by oxidation of $Co^{II}OEP$.[21] In our study, $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ and $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$ were prepared by chemical oxidation of $Co^{II}OEP$ in methylene chloride solution.

Figure 1 shows the room-temperature absorption and MCD spectra of the two-electron-oxidized products of $Co^{II}OEP$, the π-cation-radical species $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$ (Figure 1a) and $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ in methylene chloride (Figure 1b). Historically, several different, yet highly specific, features in the absorption and MCD spectral enevelopes of these two species have been taken as manifestations of the two different ground states that can be adopted by the porphyrin π-cation-radical complexes, namely, the $^2A_{1u}$ state in the case of $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ and the $^2A_{2u}$ state for $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$.[6-8] In the spectra in Figure 1, we see that the MCD bands between 350 and 450 nm, and between 540 and 670 nm, are completely different for the $^2A_{1u}$ species when compared with the $^2A_{2u}$ species. The resolved band at 660 nm in the bromide spectrum has been used as a marker for cation radicals with the $^2A_{1u}$ ground state, while the well-resolved Soret band, together with its associated *A* term, in the perchlorate spectrum has been used as a marker for the $^2A_{2u}$ ground state. These two features have been used as aids in characterizing the spectra of the horseradish peroxidase and catalase compound I species.[22] The problem in assigning the room-temperature spectra is that there are so many overlapping bands in both absorption and MCD spectra, and in comparison with MCD spectra of neutral porphyrin complexes, there is a distinct absence of *A* terms.[10,20]

Figure 2 shows the MCD spectra of $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ measured at temperatures between 5.5 and 70 K in a 2-butyl chloride–CH_2Cl_2 (1:1 v/v) glassy solution. The weak MCD *A* term indicated by a star (near 550 nm) is due to unreacted, residual $Co^{II}OEP$. The spectrum obtained at 70 K is almost identical with that measured at room temperature (Figure 1). Decrease in the sample temperature below 70 K is accompanied by a dramatic increase in MCD intensity throughout the UV-visible region. These changes are fully reversible with temperature. The dependence of the MCD intensity on the inverse of the temperature is linear over the temperature range 5.5–70 K at the 2.81-T field used. Similar spectral data were obtained for $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$. The MCD spectrum of $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$ is also temperature dependent.

While the observed spectral data measured as a function of temperature are of considerable interest, much more useful information is obtained when the purely temperature-dependent bands are separated from the temperature-independent bands. Temperature-dependent bands arise from MCD *C* terms,[15] in which the intensity is directly related to degeneracy in the ground state.[15] Figure 3 presents the intensities of the temperature-dependent components calculated for the MCD spectra of $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ (Figure 3a) and $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$ (Figure 3b), at a number of temperatures. The MCD intensity in the spectrum of $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ was also measured as a function of the magnetic field at magnetic flux densities, *B*, between 0 and 4.60 T at 4.2 K. At the highest field used at this temperature, 4.6 T, the MCD signal had not yet fully saturated, as indicated by the magnetization curves (intensity vs $\beta B/2kT$) plotted for the MCD intensity at 391 and 648 nm. It is interesting to note that many more bands are resolved in the $^2A_{1u}$ bromide spectrum at 4 K, compared with the associated room-temperature spectrum.

Discussion

The visible and UV regions in the electronic spectra of many neutral metalloporphyrins have been successfully described in terms of Gouterman's four-orbital model.[5,9,10] The curious features of the π-cation-radical absorption and MCD spectra have resulted in much discussion in the literature, initially because of the use of synthetic porphyrin π-cation-radical complexes as model compounds for the peroxidase and catalase compound I species.[6,23] Edwards and Zerner[11] have reported theoretical calculations applied to the spectra of the π-cation-radical species of metallo-

---

(22) Browett, W. R.; Stillman, M. J. *Biochim. Biophys. Acta* **1981**, *660*, 1.

(23) Browett, W. R.; Gasyna, Z.; Stillman, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 3633.

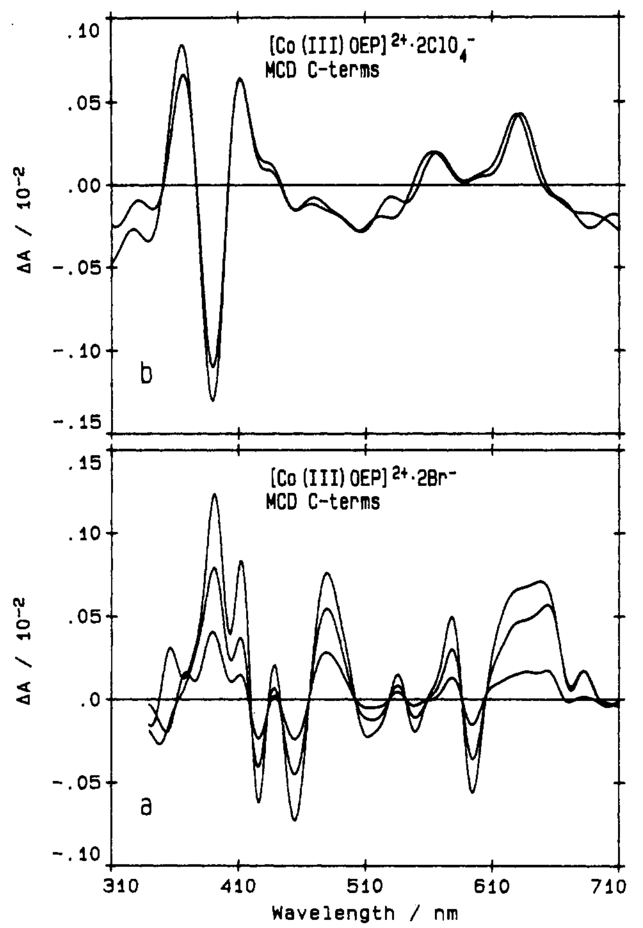

Figure 3. Temperature dependence of the MCD *C* terms of (a) $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ and (b) $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$. The spectra for $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ are shown for 5.5, 10, and 15 K, at 2.81 T, while the spectra for $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$ are for 4.2 and 10 K, at 4.6 T. The spectra were calculated by subtracting from each low-temperature spectrum the temperature-independent spectrum, which was measured at 70 K for $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ and at 100 K for $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$. The spectra were recorded for glassy solutions of the porphyrin radicals in the 2-butyl chloride–CH_2Cl_2 mixture (1:1 v/v). For presentation purposes, these spectra were smoothed by using a FFT digital filter.

porphyrins. Their calculations predicted that while there should be substantial differences between the main optical transitions of species with the $^2A_{1u}$ or $^2A_{2u}$ ground state, the excited states in each type of complex would be degenerate, which should result in Faraday *A* terms being observed. Yet, neither the room-temperature nor the low-temperature MCD spectra of $MgOEP^{\bullet +}$ ($^2A_{1u}$) or $ZnTPP^{\bullet +}$ ($^2A_{2u}$) are dominated by *A* terms,[12,13,23] although for the $^2A_{1u}$ $ZnPc^{\bullet +}$ [13] and $MgPc^{\bullet +}$ [24] species, *A* terms are observed. The MCD spectra between 400 and 720 nm of the porphyrin π cation radicals are dominated by a series of weak, positive bands, with far more bands than were predicted by theory.[11] While we have found similar, complicated MCD spectra for other porphyrin π-cation-radical species[12] (including compound I spectra of peroxidase and catalase),[22,23] we have not been able to determine why the MCD spectrum is so unusual and why there are no *A* terms present.

Our finding that the MCD spectra for *both* $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ and $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$ are temperature dependent is a new result and points directly to the presence of *C* terms that result from a degenerate ground state. It is important to note that we have observed no temperature dependence between 4.2 and 298 K in the MCD spectra of either $MgOEP^{\bullet +}$ or $ZnTPP^{\bullet +}$,[12] complexes that have the $^2A_{1u}$ or $^2A_{2u}$ ground state, respectively. Temperature independence in the MCD spectrum of ring-oxidized porphyrins is to be expected, because the ground state is an orbitally nondegenerate $^2A_{1u}$ or $^2A_{2u}$ state. The main porphyrin $\pi \rightarrow \pi^*$ transitions should still be observed, and the degeneracy in the lowest unoccupied molecular orbital, e_g, is expected to be maintained for the situation where a single electron is lost from either the a_{1u} or a_{2u} HOMO. Therefore, we expect to find *A* terms for (using the perchlorate $^2A_{2u}$ species for the illustration) Q band $= a_{1u}^2 a_{2u}^1 e_g \rightarrow a_{1u}^2 a_{2u}^0 e_g^1$ and B band $= a_{1u}^1 a_{2u}^2 e_g^0 \rightarrow a_{1u}^1 a_{2u}^2 e_g^1$, following Gouterman's four-orbital convention.[9] We clearly do not see the *A* terms predicted by this simplified scheme.

MCD *C* terms result from the presence of a degenerate ground state.[20] Fujita et al.[25] have reported that the unpaired electron on the ring is coupled into the Co(III) orbitals. As this is a spin-only coupling, the ground state remains orbitally nondegenerate and *C* terms should not be seen without further perturbations. The MCD spectrum may, however, specifically change with temperature because of effects that also occur in the excited state.

Spin–orbit coupling in the excited state can lead to a shift in the energies of the magnetic field split components of the ^2E_g excited states of the porphyrin ring, such that equivalence in the energies of the magnetic field split orbital components is lost. Transitions from the upper *spin* component of the $^2A_{1u}$ or $^2A_{2u}$ ground state will lose intensity at very low temperatures as a result of an increase in the population of the lower state due to the Boltzmann distribution across the two components of the ground state.[20]

Knowing that $ZnTPP^{\bullet +}$ and $MgOEP^{\bullet +}$ yield temperature-independent MCD spectra, we can ask under what conditions the Co(III) can couple with $P^{\bullet +}$ (P = porphyrin) that are unique and not expected for Zn(II) and Mg(II). The answer must lie with either charge-transfer states coupling to the excited π–π^* states or low-lying (d–d) states coupling to the π-cation ground state. A similar interpretation has been used by Treu and Hopfield to describe the temperature-dependent MCD spectra observed for several hemoglobin complexes.[26] A key part of our interpretation of the temperature dependence shown in Figures 2 and 3 is the location of a charge-transfer state in the region of the π^* excited states (this is not unexpected for Co(III)). The proximity of the CT state allows the spin–orbit coupling coefficient on the Co(III) to modify the energies of the individual, degenerate, π–π^* $L{\cdot}S$ states. Thus, we observe what have been termed by Piepho and Schatz[20] as "temperature-dependent *A* terms", a spectral feature that increases in intensity as the temperature drops. As this expression is a terminological contradiction (*A* terms can only be temperature independent), we must note that the bands are truly *C*-term-shaped and arise from the spin degeneracy in the ground state. Because of the manner in which the selection rules operate for a transition from a ground level to an excited-state level of the same spin, a degenerate-shaped feature is observed to dramatically intensify. The two orbitally degenerate components of the excited state are selected so that an *A*-term-like band is observed. The MCD data show that a similar interaction is present in both $^2A_{1u}$ $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ and $^2A_{2u}$ $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$.

In the case of a low-spin, but still paramagnetic, d^4 Fe(IV) (e.g. horseradish peroxidase compounds I and II),[23,27] we have described the effect of temperature on the MCD spectrum in HRP compound I as a manifestation of relatively weak spin–orbit coupling between the $S = {}^1/_2$ porphyrin π-cation-radical protoporphyrin IX group and the $S = 1$, $3d^4$ Fe(IV) metal ion, because the MCD spectrum was essentially temperature independent down to 30 K.[23] The coupled ground state in the case of the Fe(IV) π-cation-radical heme could result in an orbitally degenerate ground state, and hence the observation of *C* terms in the MCD spectrum. The coupling between an $S = {}^1/_2$ porphyrin π cation radical and an $S = 0$, $3d^6$ Co(III) metal ion is not the same because the ground states of both the ring and the low-spin d^6 Co(III) metal are orbitally nondegenerate.

---

(24) Ough, E.; Gasyna, Z.; Stillman, M. J. Unpublished data.

(25) Fujita, E.; Chang, C. K.; Fajer, J. *J. Am. Chem. Soc.* **1985**, *107*, 7665.

(26) Treu, J. I.; Hopfield, J. J. *J. Chem. Phys.* **1975**, *63*, 613.

(27) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Biochemistry* **1988**, *27*, 2503.

We can consider two CT transitions:

$$\mathrm{Co(III)} + \mathrm{P}^{\bullet+} \rightarrow \mathrm{Co(II)} + \mathrm{P}^{2+} \quad (\mathrm{Co:}\ \mathrm{d}^6 \rightarrow \mathrm{d}^7) \tag{i}$$

$$\mathrm{Co(III)} + \mathrm{P}^{\bullet+} \rightarrow \mathrm{Co(IV)} + \mathrm{P}^{0} \quad (\mathrm{Co:}\ \mathrm{d}^6 \rightarrow \mathrm{d}^5) \tag{ii}$$

For the Co(II)/Co(III) couple, the redox potential is about +0.3 V, while for the $P^0/P^{\bullet+}$ and $P^{\bullet+}/P^{2+}$ couples, the $E_{1/2}$ values are about +1.0 and +1.2 V, respectively.[1] The transition (ii) can be excluded due to the unlikely oxidation process of Co(III) to Co(IV). The resulting CT states from (i) can be written as $S = {}^1/_2$, ${}^2B_{2u}$ ($\pi \rightarrow d$), with orbital contributions ($a_{1u}{}^0$, $a_{2u}{}^2$, $b_{2g}{}^1$) for a transition from the ${}^2A_{1u}$ ground state (a similar CT state is formed for the ${}^2A_{2u}$ species).

Low-lying (d–d) states of Co(III) may also couple with the ground state of $P^{\bullet+}$. Antipas and Gouterman[28] have reported that emission intensity is quenched in both Co(II) and Co(III) neutral porphyrins and have suggested that low-lying CT or ^{3}(d–d) states may be coupling to the ground state, such that this route offers an efficient nonradiative deactivation pathway. We do not believe that this mechanism would generate the MCD intensity growth in the *C* terms in the manner that we have observed.

In summary, we suggest that the most reasonable interpretation of the temperature dependence in the MCD spectra of both $\mathrm{Co^{III}OEP^{\bullet 2+}}$ species is that spin–orbit coupling in the porphyrin excited states due to the overlap of an LMCT band modifies the energies of the pure $L{\cdot}S$ π^* states such that the individual $L{\cdot}S$ components are no longer equally separated by the magnetic field. The temperature-dependent intensity can be described in terms of spin-dependent *C* terms that result from transitions out of the lower spin component of the ${}^2A_{1u}$ or ${}^2A_{2u}$ ground state. The low-temperature MCD spectrum of $\mathrm{[Co^{III}OEP]^{\bullet 2+}(Br^-)_2}$ is the first to exhibit features characteristic of the presence of degenerate excited states.

Acknowledgment. We are grateful for financial support from the NSERC of Canada through Operating, Strategic, and Equipment Grants and the Academic Development Fund at the UWO (for an equipment grant). We wish to thank Professor Paul N. Schatz for helpful discussions. We are associated with the Centre for Chemical Physics and the Photochemistry Unit at the UWO. This is publication No. 404 from the Photochemistry Unit.

Registry No. $\mathrm{Co^{II}OEP}$, 17632-19-8; $\mathrm{[Co^{III}OEP]^{\bullet 2+}(Br^-)_2}$, 32880-79-8; $\mathrm{[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2}$, 33058-44-5.

---

(28) Antipas, A.; Gouterman, M. *J. Am. Chem. Soc.* **1983**, *105*, 4896.

Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Cluster Ions in the Electron and Chemical Ionization Mass Spectra of Transition-Metal Acetylacetonates

L. K. L. Dean, G. C. DiDonato,[†] T. D. Wood, and K. L. Busch*

Received May 24, 1988

The electron ionization mass spectra of transition-metal acetylacetonates have been recorded under conditions that maximize the abundance of cluster ions (those ions containing two or more metal atoms). Present electron ionization results obtained for copper(II), iron(III), and vanadium(III) acetylacetonates are similar to previously reported results for ions smaller than the molecular ion, but several new cluster ions of higher mass are observed. Cluster ions for zirconium(IV) and palladium(II) acetylacetonates under electron ionization conditions are reported here for the first time. The methane and ammonia chemical ionization mass spectra of transition-metal acetylacetonates are also included in this report; this represents the first application of chemical ionization mass spectrometry to this class of compounds.

Introduction

Transition-metal acetylacetonates were among the first transition-metal complexes to be studied by electron ionization mass spectrometry due to their high volatility, thermal stability, and ease of preparation.[1] Interpretation of their mass spectra has allowed a comparison of the effect of different metals, and different metal oxidation states, on the pattern of fragmentation observed in the mass spectra. The importance of changes in metal valency during fragmentation, first noted in the mass spectra of metal chlorides by Shannon and Swan,[2] was further studied and confirmed in the investigation of these compounds. Perhaps no other class of coordination compounds has been so thoroughly studied by mass spectrometry. The mass spectra of metal acetylacetonates obtained by various investigators are reasonably similar with respect to the nature and relative abundances of the ions formed.[1,3–7] Fragmentation pathways have been extensively studied. Further, high-resolution mass spectrometry has been used to confirm empirical formulas, and isotopic labeling has been used to elucidate rearrangement reactions, especially those involving hydrogen.[5,6]

The most striking feature of the electron ionization mass spectra of transition-metal acetylacetonates is the presence of cluster ions (those ions containing two or more metal atoms) at masses above that of the molecular ion. MacDonald and Shannon, who carried out the first comprehensive study of these compounds,[1] noted several cluster ion species, with some ions including three metal atoms. The origin of these ions, whether derived from dissociations of still larger gas-phase cluster species or resulting from ion/molecule reactions, was not established in these initial investigations. In addition to the formation of cluster ions, complex atom transfer reactions have been reported both for the metal acetylacetonates[1] and for complexes of metals with fluorinated β-diketonates.[8]

The question of cluster ion formation in the gas phase was later addressed thoroughly by Schildcrout.[9] The dependence of the cluster ion abundances on sample pressure, temperature, repeller potential, and ionizing energy in an electron ionization source indicated that the cluster ions are products of reactions between metal-containing fragment ions and neutral monomers of the

---

* To whom correspondence should be addressed.

[†] Present address: The Squibb Institute for Medical Research, P.O. Box 4000, Princeton, NJ 08543-4000.

(1) MacDonald, C. G.; Shannon, J. S. *Aust. J. Chem.* **1966**, *19*, 1545.
(2) Shannon, J. S.; Swan, J. M. *Chem. Commun.* **1965**, 33.
(3) Sasaki, S.; Itagaki, Y.; Kurokawa, T.; Nakashini, K.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 76.
(4) Bancroft, G. M.; Reichert, C.; Westmore, J. B. *Inorg. Chem.* **1968**, *7*, 879.
(5) Bancroft, G. M.; Reichert, C.; Westmore, J. B.; Gesser, H. D. *Inorg. Chem.* **1969**, *8*, 1012.
(6) Reichert, C.; Westmore, J. B. *Inorg. Chem.* **1969**, *8*, 1012.
(7) Holtzclaw, H. F.; Lintvedt, R. L.; Baumgarten, H. F.; Parker, R. G.; Bursey, M. M.; Rogerson, P. F. *J. Am. Chem. Soc.* **1969**, *25*, 2559.
(8) Kung, J. C.; Das, M.; Haworth, D. J. *Inorg. Chem.* **1986**, *25*, 3544.
(9) Schildcrout, S. M. *J. Phys. Chem.* **1976**, *80*, 2834.

0020-1669/88/1327-4622$01.50/0