Analyses. 1. VPC Analysis. Micellar or aqueous ketone-saturated photolysis mixtures were extracted with calibrated volumes of ethyl ether (containing an internal standard, typically hexadecane or benzophenone) and then subjected to quantitative VPC analysis. Product analyses were performed with a 3% OV-17/chrom-Q column (6 ft × $^1/_8$ in., column temperature 160–200 °C for DBK and as high as 240 °C for higher molecular weight photoinitiators). Products from scavenging by Cu^{2+} were also analyzed, relative to a standard, by using a lower column temperature (105–160 °C (10 °C/min) for detection of benzyl chlorides and benzyl alcohols). All products were identified on the basis of the known photochemistry of starting material as well as the known retention times of authentic compounds.

Homogeneous photolysis mixtures composed of an organic solvent were typically treated with standard and then analyzed directly by VPC analysis (as described above).

2. VPC/MS Analysis. For VPC/MS analysis of micellar photolysis mixtures, products were extracted with ether and the organic layer was submitted for analysis. A Finnigan 3300 with data system 6000 equipped with an OV-101 column and temperature programmed (150–200 °C) was employed using electron impact as the method of analysis.

Data Treatment. Disappearance yields and product yields from photolyses were typically measured with respect to a standard. An unphotolyzed control sample was used to determine ketone disappearances as well as ensure proper mass balance of starting materials and products.

Quantum yield or cage effect (by scavenging, see eq 2 and 6) determinations routinely involved preparation of 2–3 sets of samples per measurement. Only the averages of these analyses were used in the calculations.

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Registry No. DBK, 102-04-5; DBK-*2,2′-*$^2H_4$, 66223-95-8; DBK-*2,2′-*^{13}C, 77787-71-4; 4-Me-DBK, 35730-02-0; 4,4′-di-Me-DBK, 70769-70-9; 4,4′-di-*t*-Bu-DBK, 64321-35-3; DBK-*1*-^{13}C, 68120-92-3; 4-Cl-DBK, 35730-03-1; 4-Br-DBK, 65636-25-*1*; DBK-$^2H_{14}$, 84752-07-8; DBK-$^2H_{10}$, 84752-08-9; HDTCl, 112-02-7; DDTCl, 112-00-5; STS, 1191-50-0; SDS, 142-87-0; SDS, 142-31-4; SHS, 2207-98-9; $NaDodSO_4$, 151-21-3; $C_6D_5CD_2CO_2H$, 65538-27-4; $(PhCH_2)_2Cd$, 17051-04-6; $CdCl_2$, 10108-64-2; PNK, 31283-78-0; DNK, 51042-38-7; NaCl, 7647-14-5; $PhCH_2OH$, 100-51-6; Na_2SO_4, 7757-82-6; O_2, 7782-44-7; $CuCl_2$, 7447-39-4; ^{13}C, 14762-74-4; D, 7782-39-0; (4-methylphenyl)acetic acid, 622-47-9; benzyl chloride, 100-44-7; (4-methylphenyl)acetyl chloride, 35675-44-6; (4-chlorophenyl)acetyl chloride, 25026-34-0; (4-bromophenyl)acetyl chloride, 37859-24-8; (4-chlorophenyl)acetic acid, 1878-66-6; (4-bromophenyl)acetic acid, 1878-68-8; 4-*tert*-butylbenzyl bromide, 18880-00-7; 4-*tert*-butylbenzyl cyanide, 3288-99-1; (4-*tert*-butylphenyl)acetic acid, 32857-63-9; (4-*tert*-butylphenyl)acetyl chloride, 52629-45-5; 4-*tert*-butylbenzylcadmium, 84752-09-0; 1-naphthylacetyl chloride, 5121-00-6; 1-naphthylacetic acid, 86-87-3; 1-naphthylacetic anhydride, 5415-58-7.

Magnetic Circular Dichroism Determination of Zero-Field Splitting in Chloro(*meso*-tetraphenylporphinato)iron(III)

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Abstract: The magnetic circular dichroism (MCD) spectrum of chloro(*meso*-tetraphenylporphinato)iron(III) [FeCl(TPP)] in dilute solution in polystyrene films has been measured over the temperature range 4–300 K. The MCD spectrum of this high-spin ($S = {}^5/_2$) complex is dominated by paramagnetic effects (C terms). The MCD temperature dependence at selected wavelengths is fit, assuming contributions from three ground-state Kramers doublets at energies 0, $2D$, and $6D$, where D is the quadratic axial zero-field splitting parameter. The D values obtained are independent of wavelength and in excellent agreement with previous measurements by other techniques. MCD is thus shown to be a usable technique for the determination of zero-field splitting parameters.

Introduction

Many complexes of transition-metal ions exhibit extremely low-lying excited electronic states at energies comparable to or less than thermal energies. Such electronic-state manifolds generally arise from the effects of small perturbations on otherwise degenerate states, and the splitting of this degeneracy is referred to as zero-field splitting. For example, in cubic complexes of first-row transition-metal ions, zero-field splittings are generally caused by noncubic (e.g., tetragonal, trigonal, rhombic) distortions and/or spin–orbit coupling.

The excited electronic states of a transition-metal complex are most commonly investigated by means of optical spectroscopy. However, the direct study of excited states of a zero-field split manifold requires the use of medium- or far-infrared (IR) spectroscopy, which is complicated by competition from vibrational absorption. Zero-field splittings are consequently more often studied by other techniques that make use of the thermal accessibility of the excited states. Such techniques include magnetic susceptibility and EPR, Mössbauer and NMR spectroscopies.

We discuss here the use of magnetic circular dichroism (MCD) in the determination of zero-field splittings. The MCD of a transition arises from the perturbation of ground and excited electronic states by a magnetic field.[3] In the case of a system with zero-field splitting, the net MCD is the summed effect of transitions from each level of the zero-field split manifold. The temperature (T) dependence of the MCD is then determined in part by the Boltzmann population factors of each level, which in turn reflect the zero-field splittings.

Despite extensive use of MCD for the study of ground and excited electronic states of transition-metal ions,[4] the use of MCD for the determination of zero-field splittings has been negligible for a variety of reasons. Instrumentation permitting extensive and facile sample-temperature variation has until relatively recently been available infrequently. Systems chosen for study at cryogenic temperatures have rarely exhibited zero-field splittings in the range accessible by MCD. In some cases where zero-field splittings exist, theoretical analysis of MCD data was not un-

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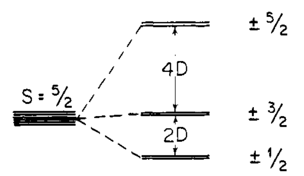

Figure 1. Zero-field splitting of the $S = {}^5/_2$ ground state of FeX(TPP).

Table I. Zero-Field Parameters for FeCl(TPP)

D, cm^{-1}	sample form	technique	ref
11.9	powder	magnetic susceptibility	6
6.5	powder	far IR	7
11.3	solution in $CDCl_3$	NMR	8
7.0	powder	Mössbauer	9
6.0	single crystal	magnetic susceptibility	10
6.9	polystyrene film	MCD	this work

dertaken because of the complexity of the system.

The system chosen for study here is the well-characterized five-coordinate ferric porphyrin complex, chloro(*meso*-tetraphenylporphinato)iron(III) [FeCl(TPP)]. To a first approximation the molecular symmetry is C_{4v} and the ground state is $^6A_1$. Due to spin–orbit coupling, this level is split into three Kramers doublets with (zeroth-order) M_S values of $\pm^1/_2$, $\pm^3/_2$, and $\pm^5/_2$. Describing the splitting by an effective Hamiltonian, DS_z^2, the $|M_s|$ $^1/_2 \rightarrow {}^3/_2$ and $^3/_2 \rightarrow {}^5/_2$ spacings are $2D$ and $4D$, respectively,[5] as illustrated in Figure 1. D is referred to as the axial (quadratic) zero-field splitting parameter. We expect the MCD of FeCl(TPP) to be the sum of the MCD of the three Kramers doublets, each weighted by a Boltzmann factor dependent on D. Study of the temperature dependence over a range where kT is comparable to the zero-field splitting will then enable D to be calculated. Previous determinations of D for FeCl(TPP) have used magnetic susceptibility[6,10] and far-IR,[7] NMR,[8] and Mössbauer[9] spectroscopies. Values obtained are summarized in Table I and range from 6.0 to 11.9 cm^{-1}.

In order to carry out MCD measurements at cryogenic temperatures, it is necessary for the sample to be in a form permitting propagation of circularly polarized light. Single crystals are only suitable when cubic or uniaxial. Randomly oriented systems can be used in the form of glasses, polymer films, pellets, etc., as long as optical quality is adequate. In this work we have chosen to use samples in which the complex is in dilute solution in a polymer matrix. This technique has been used previously in MCD studies[11] and is of quite general applicability.

Our study shows that MCD is a usable technique for the determination of zero-field splittings and provides a new measurement of D in FeCl(TPP).

Theory

The MCD of a molecule whose ground-state manifold consists of three Kramers doublets can be written as

$$\Delta A(\nu) = \{\sum_{i=1}^{3}(a_i + b_i + c_i/kT)\alpha_i\}H \tag{1}$$

where i sums over the three Kramers doublets, a_i, b_i, and c_i are the contributions of $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ terms to the spectrum at the frequency ν, and α_i is the fractional population of the ith state. Equation 1 follows from the rigid shift equation[3] but is considerably more general.[12] The most important approximations made in eq 1 are that Zeeman effects within the ground-state manifold are linear in H and that Zeeman splittings are $\ll kT$.

In the $S = {}^5/_2$ FeCl(TPP) molecule under study here, we have found that $\mathcal{C}$ terms are almost exclusively responsible for the MCD at the frequencies where temperature dependence has been measured. Consequently, we further approximate eq 1 to the form

$$\Delta A(\nu) = \left\{\sum_{i=1}^{3}\frac{c_i}{kT}\alpha_i + d\right\}H \tag{2}$$

where the diamagnetic ($\mathcal{A}$ and $\mathcal{B}$ term) contributions have been reduced to a single constant. The justification for this procedure is that, a posteriori, it works. In addition, we use the axial, quadratic approximation to the zero-field splitting, discussed above, whence

$$\begin{aligned}\alpha_1 &= 1/(1 + e^{-2D/kT} + e^{-6D/kT})\\ \alpha_2 &= e^{-2D/kT}/(1 + e^{-2D/kT} + e^{-6D/kT})\\ \alpha_3 &= e^{-6D/kT}/(1 + e^{-2D/kT} + e^{-6D/kT})\end{aligned} \tag{3}$$

Further, we assume that the c_i and d parameters are independent of temperature. This implies the assumption that spectral band shapes are independent of temperature over the range under consideration.

There are two limiting situations in which eq 2 becomes simply linear in $1/T$. First, if $D \gg kT$, only the lowest Kramers doublet is populated and

$$\Delta A = \{c_1/kT + d\}H \tag{4}$$

Second, if $D \ll kT$, all three Kramers doublets are equally populated and

$$\Delta A = \left\{\frac{c_1 + c_2 + c_3}{3kT} + d\right\}H \tag{5}$$

In neither limit is the MCD dependent on D. The use of MCD to determine D then rests on the accessibility of the temperature range where $D \sim kT$. With presently available cryogenic systems D values $\lesssim 1$ cm^{-1} are thus not capable of measurement. On the other side, D values $\gtrsim 100$ cm^{-1} will also be difficult to measure without use of temperatures higher than ambient.

Equation 2 could be further approximated by the use of explicit, calculated values for the c_i parameters, under the assumption of specific excited-state assignments. The complexity of the analysis of the Fe(III) porphyrin spectrum, which involves both $\pi \rightarrow \pi^*$ and charge-transfer excitations and must include vibronic and spin–orbit effects, currently renders such calculations insufficiently reliable for the practical determination of D values. However, it is worth noting that, under the assumption of wholly in-plane (x, y) polarized electric dipole transition moments for transitions originating in the $^6A_1$ state, there are no $\mathcal{B}$ terms arising from the mixing of the ground set of Kramers doublets, since within a $^6A_1$ manifold the out-of-plane (z) component of the magnetic moment operator is diagonal in M_s. Such $\mathcal{B}$ terms would in general be comparable in order of magnitude to $\mathcal{C}$ terms when $kT \sim D$ and would thus require inclusion in analysis of data. Since z-polarized intensity is almost always weak or negligible in both porphyrin and heme protein spectra,[13] this is very likely to be true in FeCl(TPP). This explains the absence, and justifies the neglect in eq 2, of large diamagnetic contributions.

In the molecule under study here the effects of deviations from axial symmetry (intra- or intermolecular in origin) on the ground electronic state are shown by EPR to be negligible. This is not necessarily equally true of the excited electronic states. This is not important in our analysis, however, since the assumption of axial symmetry only enters into eq 1–3 via the assumption of the

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axial zero-field splitting effective Hamiltonian for the ground state, which leads to the α_i expressions of eq 3.

Experimental Section

FeCl(TPP) was prepared in Professor C. A. Reed's laboratory at the University of Southern California following a literature procedure[14] with minor modifications. The absorption spectrum [λ_{max} (ϵ) = 372 nm (4.71 $\times$ 10^4 cm^{-1} mol^{-1} L), 418 (1.08 $\times$ 10^5), 507 (1.18 $\times$ 10^4), 572 (5.0 $\times$ 10^3), and 685 (3.1 $\times$ 10^3) in toluene] is in good agreement with literature data.[14] Samples for MCD were in the form of dilute solutions in polystyrene films. A film was prepared by dissolving FeCl(TPP) in a solution of polystyrene (Aldrich, catalog number 18,242-7) in toluene, placing the resulting solution on a glass plate and slowly evaporating to dryness. Films used in this work had thicknesses of approximately 50 μm and were around 1 mM in FeCl(TPP). The exact thicknesses and concentrations were not accurately measured since their knowledge is not required for data analysis. Despite the thinness of the films, they can be easily removed from the glass plate and handled without loss of integrity. For low-temperature spectroscopy a rectangular section of a film was mounted on a copper sample holder by taping along one edge.

Absorption spectra in the range 4–300 K were measured by using an Oxford Instruments CF204 flow cryostat system and a Cary 17 spectrometer. MCD spectra over the same temperature range were measured by using an Oxford Instruments 50 kG (5 T) Spectromag 3 top-loading, split-coil magnet system and a Jasco J-500C spectropolarimeter.[15] In both cryogenic systems the copper sample holder is screwed onto the end of a sample probe and is in helium gas at atmospheric pressure. Temperature variation is accomplished by adjustment of helium gas flow rate, in the CF204 through the heat exchanger and in the SM3 through the sample compartment, and a heater. Temperature measurement and control are accomplished by an Oxford Instruments DTC-2 temperature controller, connected to a CLTS thermometer and the heater. In the CF204 and SM3 the thermometer and heater are mounted on the heat exchanger and sample probe, respectively. The temperature differentials between sample and thermometer positions have not been studied. In the CF204 these may be several degrees, but accurate temperatures were not required in the absorption spectroscopy studies here. In the SM3 the thermometer and sample are in the same column of helium gas and are expected to be very close in temperature. The thermometer in the SM3 was recalibrated at the beginning of every MCD experiment.

It is essential in MCD measurement on solid samples to ensure that the sample is isotropic and strain-free. All samples used in this work were investigated prior to MCD measurement by comparing the CD spectrum of a nickel tartrate solution (obtained by mixing equal volumes of solutions 0.24 M in $NiSO_4$ and 0.36 M in potassium *d*-tartrate) placed before and after the SM3, in which the polymer film was already mounted and cooled in liquid helium temperature. Sample birefringence and strain would lead to depolarization of the light beam, which would affect the nickel tartrate CD when positioned after the sample, but not before. No evidence for depolarization effects was obtained in any experiment, showing that, at least at the path lengths used, the films were of excellent optical quality. Parenthetically, it is worth noting that these experiments also show the absence of observable strain in any of the windows of the SM3.

MCD measurements were carried out in two stages. First, the field (H) dependence of the MCD was measured at ~5 K in order to determine the range over which the MCD is accurately linear in H. Second, at a fixed field within the linear range, the temperature dependence was measured over the range 4–250 K. All MCD measurements are carried out at a spectral band width of 2 nm; narrower band widths led to no change in the spectra.

EPR measurements were carried out on samples used for MCD measurements using a Varian E-12 spectrometer and an Oxford Instruments ESR-9 flow cryostat. Samples were placed in a cylindrical quartz tube. Temperature measurement and control used a thermocouple thermometer and an Oxford Instruments DTC-2 temperature controller.

Absorption and MCD spectra were digitized and replotted by using a Calcomp plotting package.

Results

The absorption and MCD spectra of FeCl(TPP) in polystyrene near room and liquid helium temperatures are shown in Figures 2 and 3. All data shown were obtained on the same sample. Absorption and MCD are plotted in terms of A and ΔA (absorbance and differential absorbance). An approximate value of cl, where c is the concentration of FeCl(TPP) and l is the film pathlength, is given in the figure captions and can be used to convert the data to ϵ and $\Delta\epsilon$ values. The cl value is based on the assumption that the Soret band (~420 nm) absorption intensity at room temperature is identical in the film and in toluene solution and that Beer's law is valid. We have tested the latter in toluene solution and found no deviation up to a 1 mM concentration. The H dependence of the MCD at two wavelengths and at 5.3 K was measured up to 50 kG and is shown in Figure 4. Significant nonlinearity occurred at higher fields. The data shown in Figures 2 and 3 were obtained at a field (10.3 kG) within the linear region.

The absorption spectrum of FeCl(TPP) in polystyrene films is almost identical with that in toluene solution; band maxima are

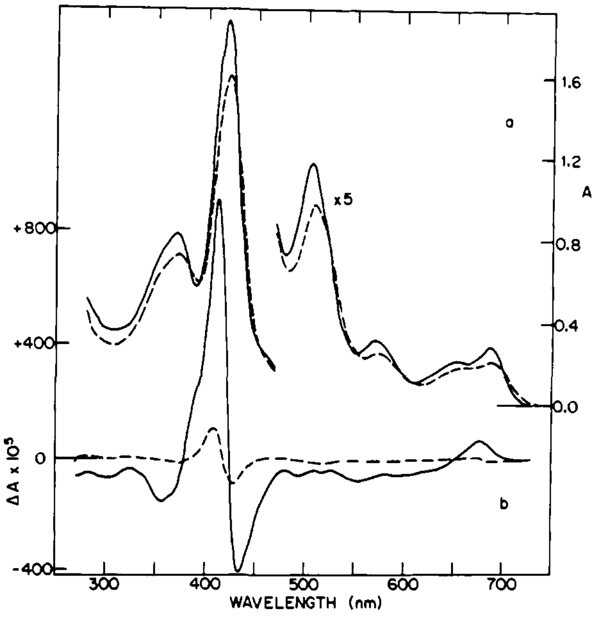

Figure 2. Absorption spectrum (a) at 6.3 (—) and 295 K (- - -) (right-hand scale) and MCD (b) at 5.3 (—) and 230 K (- - -) (left-hand scale) of FeCl(TPP) in polystyrene. In b the magnetic field is +10.3 kG. Assuming ϵ of the Soret band is identical with that of FeCl(TPP) in toluene, A and ΔA can be converted to ϵ and $\Delta\epsilon$ by using cl = 1.48 $\times$ 10^{-5} cm mol liter^{-1}.

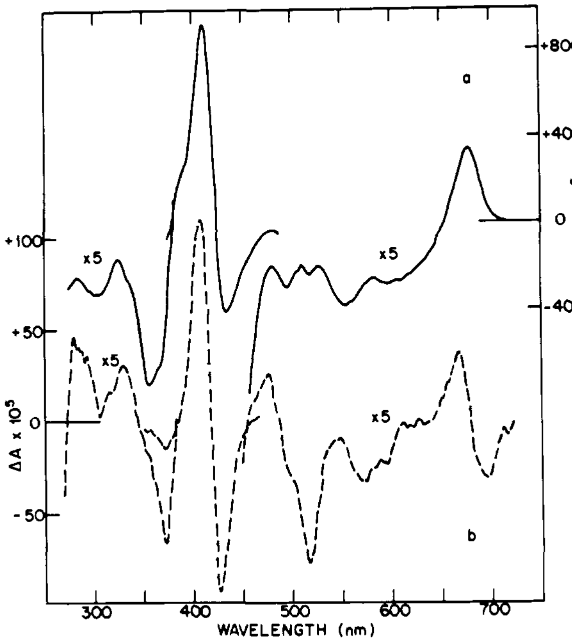

Figure 3. MCD of FeCl(TPP) at (a) 5.3 (right-hand scale) and (b) 230 K (left-hand scale). The magnetic field is +10.3 kG. A and ΔA can be converted to ϵ and $\Delta\epsilon$ by using cl = 1.48 $\times$ 10^{-5} (Figure 2).

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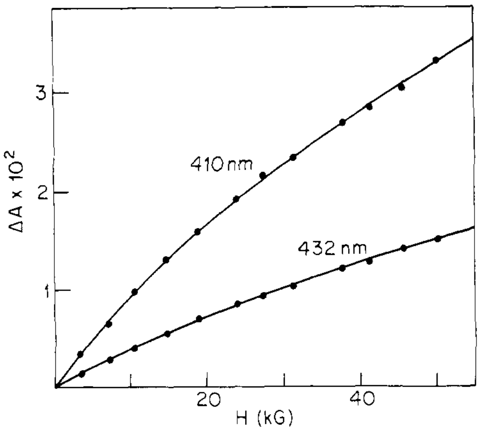

Figure 4. MCD field dependence of FeCl(TPP) at 5.3 K and at 410 and 432 nm.

shifted by at most 3–4 nm. The EPR at liquid helium temperatures of FeCl(TPP) in polystyrene films was axial in shape, with $g_\perp \approx 6.06$ and $g_\parallel \approx 2.01$, and showed no significant impurity signals. The chemical integrity of FeCl(TPP) in the polystyrene environment is thus clearly maintained, and there is no reason to invoke deviations from axial symmetry in the ground electronic state. There is no evidence for paramagnetic impurities that might contribute to the paramagnetic MCD spectrum.

Figures 2 and 3 demonstrate that the MCD is strongly temperature dependent and that the largest MCD is in the Soret band region. We have therefore used the MCD extrema in the Soret band region for detailed study of the temperature dependence of the MCD. The results obtained are shown in Figure 5.

It is immediately apparent that, while at high temperatures the MCD is approximately linear in $1/T$, in the lower part of the temperature range the MCD becomes nonlinear in $1/T$. This clearly demonstrates the contribution of multiple ground-state levels. We have fit eq 2 and 3 to the MCD data using a trial-and-error procedure. The initial fitting procedure involved determining approximately c_2 and c_3 relative to c_1 over a wide range of D. The low-temperature region is dominated by contributions from c_2 and c_1 and an appropriate value of c_2/c_1 was chosen to fit the curvature of the data in this region. The residual intensity that occurs at higher temperatures (above ~50 K) was then fit with an approximate c_3/c_2 value. Following the definition of the domain in parameter space yielding visually acceptable fits, a fine grid of values of the four parameters was surveyed, and those yielding a minimum least-square deviation from experimental data obtained. Our best fits to the MCD data are shown in Figure 5, together with the contributions of the individual ground-state sublevels. The differences between theoretical fits and experiment are within experimental error. The contributions of three ground-state levels are required to fit the data acceptably, showing that the ground state is (at least) $S = {}^5/_2$. Two levels are inadequate and exclude the academic possibility that $S = {}^3/_2$. The values of D obtained from the MCD data at two different wavelengths are in excellent agreement. The average value obtained is 6.9 cm^{-1}.

Discussion

Our results for FeCl(TPP) demonstrate the viability of the approach employed. First, the observed temperature dependence over a wide range is satisfactorily reproduced by the theoretical model, and the D values obtained are independent of the wavelength selected, within experimental error. We believe that the differences between experiment and theory are nonsystematic, experimental errors, most likely due to limitations in sample-temperature control. Second, the results obtained are in acceptable agreement with values derived by other methods (Table I). These latter vary quite widely, so this is not a precise criterion.

In comparing our D value with those of other workers, there are several possible explanations for the observed differences: experimental errors, inadequate theoretical models used to fit data, or differing sample conditions. It is quite conceivable that real differences in D value exist between dilute solution and pure solid (single crystal, powder) conditions. While in the case of tetraphenylporphyrin complexes, the phenyl groups act to separate adjacent porphyrin moieties, it is well-known that porphyrins are strongly interacting molecules. However, this cannot be the entire story, since measurements of D on pure FeCl(TPP) range from 6.0 to 11.9 cm^{-1}, indicating errors or inadequacies in at least some of the experimental methods employed. Mitra et al.[16] have shown the zero-field splittings determined by Maricondi et al.[6] for several FeX(TPP) complexes using average magnetic susceptibility data to be in error. The proton NMR chemical shifts used[8] to deduce D in FeCl(TPP) have recently been fit with apparently equal accuracy by using the D value (6.0 cm^{-1}) obtained from single-crystal magnetic anisotropy data.[17] It would appear therefore that the larger values, 11.9 and 11.3 cm^{-1}, obtained from powder susceptibility[6] and NMR[8] measurements, are likely to be in error. All remaining measurements lie between 6.0 and 7.0 cm^{-1} and are identical within quoted experimental errors. Our MCD technique is thus in excellent agreement with the far-IR, single-crystal magnetic anisotropy, and Mössbauer results. A more conclusive test of the relative reliability of each method would be provided by a combined study on a single material. For example, given the current availability of very high sensitivity susceptometers, it should be possible to make average susceptibility, Mössbauer, and MCD measurements on a single doped-polymer sample, and this would be of considerable interest.

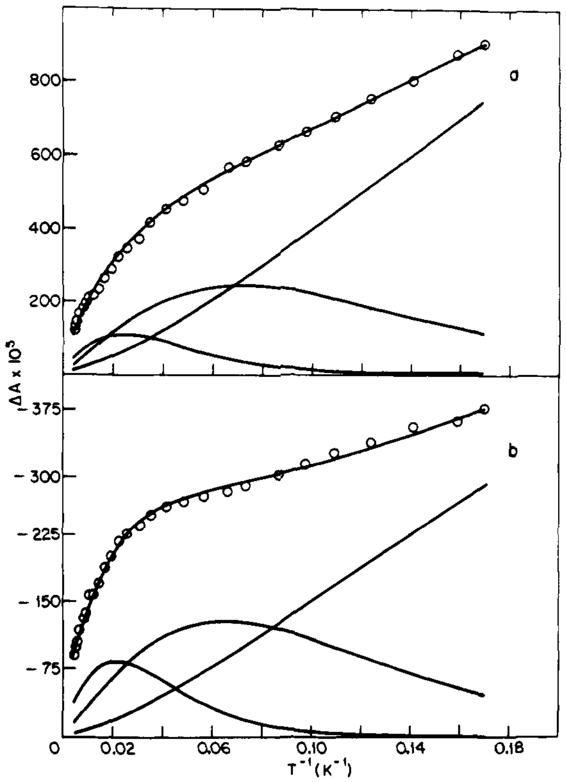

Figure 5. MCD temperature dependence of FeCl(TPP) at (a) 410 and (b) 432 nm. Circles are experimental points. Solid lines are best fits to the data and the individual contributions of the $|M_s| = {}^1/_2, {}^3/_2$, and ${}^5/_2$ levels thereto: (a), $D = 6.5$ cm^{-1}, $c_1 = 2.0$, $c_2 = 7.0$, $c_3 = 13.7$; (b) $D = 7.2$ cm^{-1}, $c_1 = -0.7$, $c_2 = -2.7$, $c_3 = -12.2$ (all c_i values in 10^{-6} cm^{-1} G^{-1}).

An important aspect of the MCD method is that it contains contributions from all three Kramers doublets. As seen from Figure 5 and as verified by direct trial fitting, it would be impossible to fit the MCD temperature dependence at the wavelengths used without the third level being included. Thus, the data

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are inconsistent with a $S = {}^3/_2$ ground state. This does not prove that $S = {}^5/_2$, of course, only that $S = {}^5/_2$ is adequate and there is no reason to postulate $S > {}^5/_2$.

The MCD of FeCl(TPP) at room temperature in benzene solution and over the temperature range 310–79 K in a poly(methyl methacrylate) film have been reported previously.[18,19] These spectra are very similar in form to those obtained in our studies. However, the previous work did not involve a sufficient number or range of temperatures to enable useful comparison of the temperature dependence. Our work clearly demonstrates that the observation of the effects of the zero-field splitting on the MCD temperature dependence, and the determination of D therefrom, requires measurements below liquid nitrogen temperatures.

The detailed assignment of the transitions observed in the MCD spectrum of FeCl(TPP) has not been pursued in the present work. At a minimum, porphyrin $\pi \rightarrow \pi$ and porphyrin $\pi \leftrightarrow$ Fe d charge-transfer excitations are present, and these are intermixed by configuration interaction. Further, the temperature dependence of the MCD, which has been shown in this work to be large, arises from the incursion of spin–orbit coupling, since without the latter spin degeneracy does not contribute to MCD and the molecule has an effectively nondegenerate state. Lastly, vibronic effects, both transition-intensity-inducing and Jahn–Teller effects, are substantial in porphyrins. The analysis of the MCD of FeCl(TPP) is therefore a substantial challenge. Analysis of the high-temperature MCD data published earlier has been reported.[18,19] It remains to be demonstrated that this analysis successfully predicts the temperature dependence of the MCD to liquid helium temperatures, which is a sine qua non of a viable theory.

Conclusion

We have shown that the use of temperature-dependent MCD to measure zero-field splittings is practicable. This should be generally the case when such splittings are in the 1–100-cm^{-1} range, i.e., neither too small ($\lesssim 1$ cm^{-1}) nor too large ($\gtrsim 100$ cm^{-1}) to permit the MCD to be measured over a temperature range where kT spans the zero-field splittings. The method relies on the MCD parameters of the populated states being different, and its sensitivity increases with the degree of difference. It is phenomenological, in that the MCD parameters for individual transitions are not calculated a priori but are left as adjustable parameters. It is necessary therefore to confirm the viability of the analysis by making use of multiple wavelengths, demonstrating that the zero-field splitting parameters are independent of the wavelength selected and the MCD parameters determined. However, the absence of any theoretical calculation, requiring excited-state wave functions and transition moments, vastly enlarges the generality of the method.

In the case studied here, the paramagnetic, $\mathcal{C}$ term, MCD contributions are dominant. This will not always obtain, and the inclusion of $\mathcal{A}$ and $\mathcal{B}$ terms will then be required, somewhat complicating the analysis. Although it is generally expected that $\mathcal{B}$ terms are much smaller than $\mathcal{C}$ terms at low temperatures, it is important to recognize that $\mathcal{B}$ terms arising from magnetic-field-induced mixing of the zero-field split levels can in principle be very large, due to the smallness of their spacing. In the specific case where none of the ground-state manifold is degenerate, only $\mathcal{B}$ terms can occur, of course.

In principle, an identical approach could be employed, using the absorption spectrum in place of the MCD spectrum. The method of choice depends entirely on the variation of absorption and MCD among the zero-field split levels. In FeCl(TPP) the absorption spectrum varies very little with temperature, and those changes occurring are at higher temperatures and are typical band-shape temperature variations originating in vibrational effects. Clearly, at the wavelengths studied, to a good approximation the absorption of each Kramers doublet is identical. In this case, therefore, MCD is vastly superior to absorption in sensitivity to the zero-field splitting, and this can be expected to be quite generally true.

In comparison to other methods for determining zero-field splittings, MCD has several advantages. First, it will generally be possible to study molecules in dilute solution, where the problems of intermolecular interactions occurring in pure crystals are avoided. For reasons of sensitivity, magnetic susceptibility and far-IR studies are most usually carried out by using single crystals or powders. Second, as a spectroscopic phenomenon it avoids the difficulties arising from impurities that plague bulk phenomena, notably magnetic susceptibility. Third, it is not sensitive to relaxation effects, which complicate the use of EPR and NMR. Fourth, it is not limited to compounds containing special elements, as is Mšsbauer spectroscopy.

Lastly, what are the applications of zero-field splittings? First, in systems simple enough to attract thorough theoretical analysis, the zero-field splittings define level separations that must be explained (or fit) by theory, as do the transition energies observed by optical spectroscopy. They therefore serve to define ligand-field theoretical parameters and in many cases are a sensitive probe of one or more parameters (e.g., a tetragonal distortion parameter or a spin–orbit coupling constant). Second, in more complex systems they can be used as an empirical corollary of a structural environment, which can in principle serve as one of the fingerprints of this environment. For example, in the comparison of synthetic analogue complexes with protein-bound metal-containing moieties, an acceptable model must mimic not only optical absorption bands, EPR g values, and so on, but also the experimental zero-field splittings. Third, the *existence* of zero-field splittings in itself provides some information. For example, for a spin-degenerate, orbitally nondegenerate ground-state multiplet, the number of zero-field levels depends on the spin degeneracy; in turn, the demonstration of the minimum number of levels required to interpret the MCD data determines the minimum acceptable spin degeneracy. Thus, the elucidation of the gross nature of the ground state can be an outcome of the measurement of zero-field splittings.

Applications of temperature-dependent MCD to the study of electronic ground states of metal ions and clusters in inorganic compounds and metalloproteins are ongoing in our laboratory. In particular, studies of the zero-field splitting in other FeX(TPP) complexes and in ferric hemoproteins are in progress.

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