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Analysis of the Absorption and Magnetic Circular Dichroism Spectra of Zinc Phthalocyanine and the π -Cation-Radical Species $[\text{ZnPc}(-1)]^{+\bullet}$

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The first detailed band envelope deconvolution analyses of the absorption and magnetic circular dichroism (MCD) spectra are reported for neutral and oxidized complexes of zinc phthalocyanine (ZnPc) with cyanide (CN^-), imidazole (Im), and pyridine (py). The spectra were recorded for the complexes in solution at room temperature. The deconvolution results are compared with theoretical calculations of the energies and degeneracies of the excited states in neutral phthalocyanines reported by Gouterman and co-workers. The use of both absorption and magnetic circular dichroism spectra in the deconvolution calculations greatly improves the reliability of the band parameters obtained. The analyses of the spectra of the unoxidized complexes shows that there are five degenerate transitions between $14\,000\text{ cm}^{-1}$ and the solvent cutoff at $45\,000\text{ cm}^{-1}$; these bands (in cm^{-1} (nm)) are centered near $14\,910$ (671), $27\,150$ (368), $29\,780$ (336), $35\,440$ (282), and $40\,650$ (246) in $\text{ZnPc}(\text{Im})$ and are assigned, by comparison to the theoretical calculations, as transitions to the Q, B, N, L, and C states, respectively. The absorption and MCD spectra of the oxidized species are much more complicated. There are four clearly resolvable transitions (in cm^{-1} (nm)) in the absorption spectrum of the π -cation-radical species $[\text{ZnPc}(-1)(\text{Im})]^{+\bullet}$, centered at $12\,170$ (822), $14\,010$ (714), $19\,550$ (511), and $31\,520$ (317). Complete deconvolution of the absorption and MCD spectra requires 19 bands. The analysis shows that the transition near $19\,500\text{ cm}^{-1}$ is nondegenerate, while the transitions at $12\,170$, $14\,010$, and $31\,520\text{ cm}^{-1}$ are degenerate; two further degenerate bands are located at $27\,000$ and $35\,990\text{ cm}^{-1}$. The band at $14\,010\text{ cm}^{-1}$ (714 nm) is assigned as the Q band of the π -cation-radical species, while the B, N, and L transitions are associated with bands at $27\,000$, $31\,520$, and $35\,990\text{ cm}^{-1}$, respectively.

Introduction

The chemical and spectroscopic properties of phthalocyanines and porphyrins have long been studied as models of the heme proteins and chlorophylls.¹⁻¹² The development of photochemical techniques with these molecules, which can be used to carry out both photocatalysis and photoinduced redox chemistry, has been particularly exciting.^{1-5,7-9,13,14} We have recently investigated photoinduced charge separation in donor-acceptor complexes as part of the development of a solar cell that is based on using a porphyrin or phthalocyanine electron donor coupled to a quinone acceptor (where the abbreviation for the complete molecule is PQ).¹⁵ In order to examine the photochemical properties of a range of potential donors before the acceptor is chemically attached, we have studied the photooxidation of isolated ring compounds.^{13,14,16,17} In a preceding paper¹⁸ we reported the quantitative formation of the ring-oxidized $[\text{ZnPc}(-1)]^{+\bullet}$ species in solution, using both photochemical and electrochemical techniques.

The preparation of this stable π -cation-radical species in solution afforded us an excellent opportunity to compare, in some detail, high-quality optical spectra, both absorption and magnetic circular dichroism, of neutral and oxidized ZnPc complexes. We have noted during our studies of the spectroscopic properties of metallophthalocyanines that, despite the large numbers of optical spectra that have been published for phthalocyanine complexes, there have been few assignments reported that relate a majority of the bands actually observed in the absorption spectrum to the theoretically calculated electronic-state picture of Gouterman et al.¹⁹ In particular, the construction of the broad envelope of bands traditionally called the Soret band is generally not well-known. Although detailed absorption²⁰⁻²² and magnetic circular dichroism^{23,24} spectra have been described for phthalocyanines in the solid state (as thin films), these spectra have been measured for the α , β , and x phases and are, therefore, extensively broadened by Davydov coupling effects.²¹⁻²⁴ This means that the spectra do not closely resemble those obtained from solutions.

The use of the optical spectra of both the neutral and oxidized complexes of ZnPc in solution, obtained under similar experimental conditions, is an ideal starting point for an analysis of the components that contribute to the observed intensity in the spectra of metallophthalocyanines in general, because no charge-transfer transitions are to be expected at low energies. The analysis of the spectral data of the ZnPc and $[\text{ZnPc}(-1)]^{+\bullet}$ complexes will provide information on the number and degeneracies of, solely, ring $\pi \rightarrow \pi^*$ transitions for the neutral complexes and $\pi \rightarrow \pi^*$

and $\pi \rightarrow \pi$ transitions for the oxidized complexes. These results can then be used with metallophthalocyanines where charge-transfer transitions complicate the state picture. As is immediately apparent from an inspection of the spectral data of the oxidized π -cation-radical species,¹⁸ a great many transitions are responsible for the absorption and MCD envelopes. In order to begin the assignment of such complicated data, we carried out deconvolution calculations on the inherently more straightforward spectra of the neutral species. The results of these calculations are reported in the first part of this work. We use the appearance of A terms to identify degenerate transitions in the MCD spectra. While moment calculations provide the only accurate values of the magnetic moments of excited states (from the A/D values), "band fitting" or deconvolution calculations are the only way to access the transitions responsible for bands that overlap to any extent. A/D values will, under these conditions, be of the correct sign, but the magnitudes are expected to be only relatively correct when

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compared with those of other transitions of similar origin.

The data from calculations carried out on neutral ZnPc species can then be used to aid in the analysis of the more complicated spectra of the π -cation-radical species. In the second part of the paper, we report our analysis of the absorption and MCD spectra obtained for the π -cation-radical $[\text{ZnPc}(-1)]^{+\bullet}$ species. We discuss the results of our deconvolution calculations in terms of the state pictures obtained from the theoretical calculations of Gouterman and co-workers for neutral phthalocyanines,²⁵ Minor et al. for oxidized phthalocyanines,²⁰ and Edwards and Zerner for oxidized porphyrins.²⁶ As will become apparent in the discussion below, the inclusion of the MCD data in the deconvolution calculations is the only way that the parameters obtained from the calculations can be used with any degree of confidence in several complicated cases.

Magnetic circular dichroism spectra can be used to provide not only excited-state magnetic moment data but also important additional assignment criteria. The band envelope in the MCD spectrum comprises intensity from three main sources, known as Faraday *A*, *B* and *C* terms,²⁷ each of which results in a distinctive feature in the spectrum. Briefly, *A* terms arise from degeneracy in the excited state and result in a derivative shape being observed, *B* terms arise from field-induced mixing of states, and *C* terms arise from degeneracy in the ground state. *A* and *B* terms are temperature-independent, while *C* terms are temperature-dependent; the *B*-term intensity sums to zero across all bands.²⁷ Qualitative assignments of MCD spectra are often relatively straightforward for the spectra of highly symmetric complexes with nondegenerate ground states, because the derivative-shaped *A* terms centered on band centers can be readily distinguished from the *B* terms.²⁷⁻²⁹ Quantitative analysis of MCD data rests on either the method of moments for isolated transitions,^{27,30} where the zeroth and first moments are calculated directly, or band envelope deconvolution, where bands of a fixed shape are fitted to the experimental envelope.²⁷ This latter method requires a careful determination of the type of transition that is responsible for the observed intensity. It is, however, the only way to obtain meaningful quantitative information from spectra that include overlapping bands.

Experimental Section

Materials and Methods. The preparation of the unoxidized ZnPc and the one-electron-oxidized π -cation-radical species, both electrochemically and photochemically, was described in a previous paper.¹⁸ Imidazole (Im; Fisher) and sodium cyanide (NaCN; Fisher) were used without further purification; pyridine (py; Baker, reagent) was freshly purified before use.

Spectroscopic Measurements and Analysis. Absorption spectra were obtained with Cary Model 219 and 17 spectrophotometers. Molar extinction coefficients for ZnPc(CN⁻) ($\epsilon_{670} = 235\,000\text{ L mol}^{-1}\text{ cm}^{-1}$), ZnPc(Im) ($\epsilon_{670} = 178\,000\text{ L mol}^{-1}\text{ cm}^{-1}$), ZnPc(py) ($\epsilon_{670} = 240\,000\text{ L mol}^{-1}\text{ cm}^{-1}$), and ZnPc ($\epsilon_{670} = 300\,000\text{ L mol}^{-1}\text{ cm}^{-1}$) were determined in DMA and used to calculate the concentration of ZnPc in solution. MCD spectra were obtained at room temperature with a JASCO J500 C spectropolarimeter controlled by an IBM Instruments S9001 computer using the computer program CDSCANS,³¹ at a field of 5.5 T from an Oxford Instruments SM2 superconducting magnet. The instrument was calibrated by using aqueous solutions of Co(SO₄), where the intensity of the negative band at 510 nm was taken as $\Delta\epsilon_M = -1.897 \times 10^{-2}\text{ L mol}^{-1}\text{ cm}^{-1}\text{ T}^{-1}$.

Low-temperature MCD spectra of the $[\text{ZnPc}(-1)(\text{Im})]^{+\bullet}$ species were obtained from a glass made by plunging a solution of the ZnPc(-1) complex (dissolved in a 1:1 mixture of 2-chlorobutane and methylene chloride) into liquid helium held in the sample compartment of an Oxford Instruments SM4 superconducting magnet.

The MCD and absorption data were fitted with Gaussian shapes by using the program SIMPFIT.^{32a} This program utilizes a Simplex routine for the MCD spectra and a standard, least-squares routine for the absorption spectra. The moment data were calculated by direct integration of the digitized absorption and MCD data. The spectral data were manipulated and plotted on an HP 7550A digital plotter using the spectral data base management program Spectra Manager.^{32b}

Results and Discussion

Although a great many spectra of metallophthalocyanines have been reported,^{28,29,33-37} few band envelope analyses are available. While estimation of the energy of the band center directly from the spectrum is useful, there is no assurance in optical spectra as complicated as those observed for many MPc complexes that the transitions responsible for all of the intensity actually have energies represented by the various maxima measured directly from the spectra. Additionally, the total number of transitions frequently cannot be estimated with any degree of accuracy. Thus there have been few attempts to align spectral data with the theoretically calculated spectra derived from calculations of the energies of the lowest lying excited states.^{12,19}

Characterization of the spectra of the π -cation-radical species of metallophthalocyanines is even more difficult, partly because so few spectra have been reported for samples in solution and partly because the spectra are so complicated. Thus it has not been possible to establish trends that relate such variables as temperature, solvent, axial ligation, and central metal to the energies and intensities of the individual bands in the spectrum. Only Minor et al. have recently compared the spectral data of π -cation and π -anion species with a theoretically predicted state picture.²⁰

We discuss the optical spectra of ZnPc and $[\text{ZnPc}(-1)]^{+\bullet}$ in detail in this paper, because these data represent the simplest of all MPc spectra. Oxidation of ZnPc to form the π -cation-radical species is known from cyclic voltammetry (CV) studies.^{18,38} This results in partial occupation of a highest occupied molecular orbital of ²A_{1g} symmetry.^{19,25,39,40} Oxidation of ZnPc in the solid state to form the π cation radical has been reported with use of both chemical and electrochemical techniques.^{41,42} However, solid-state spectra of the oxidized phthalocyanines are quite different when compared with the solution spectra, due to the extensive intermolecular (Davydov) coupling effects described above for the neutral phthalocyanines.^{20,23,24} This makes the assignment problem very difficult for such species, where numerous overlapping bands are to be expected.

One of the requirements for the analysis of the absorption spectrum of the π -cation-radical species has been the necessity to obtain very good spectra, in solution, in solvents that do not absorb highly in the UV region. The phthalocyanines are notoriously insoluble in many common solvents and, especially, in those useful in the preparation of the π -cation species. Indeed, very few absorption spectra of any oxidized MPc species have been published and almost no MCD data are available. However, in a previous paper,¹⁸ we describe the photochemical and electrochemical preparation of $[\text{ZnPc}(-1)]^{+\bullet}$ in methylene chloride solutions, a solvent that allows the measurement of absorption and

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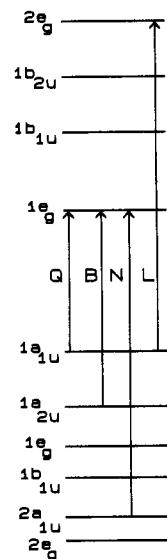


Figure 1. Molecular orbitals of the phthalocyanines. The order of the orbitals has been adopted from ref 20.

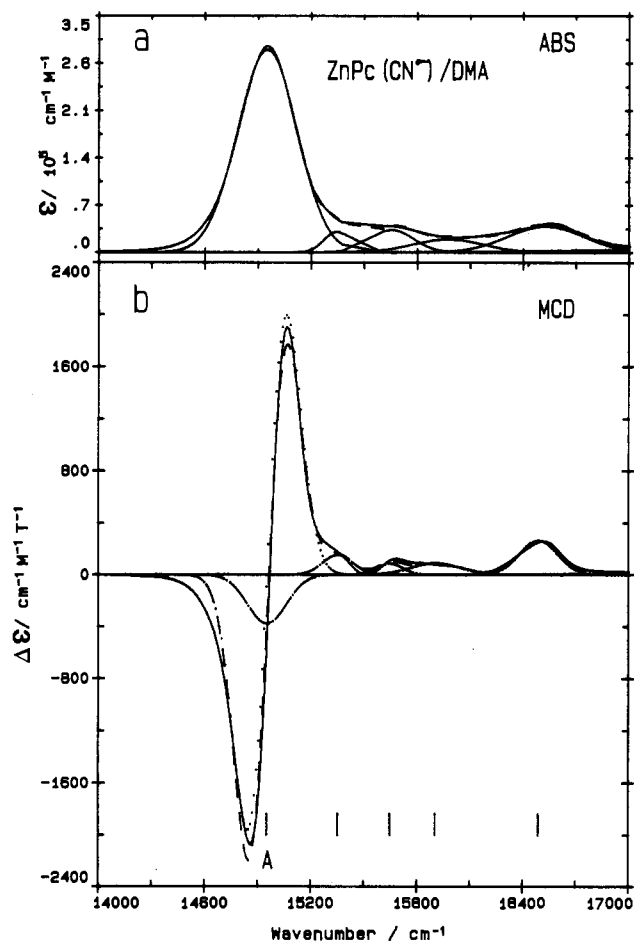


Figure 2. Band analysis for ZnPc(-2) with added CN⁻ ligand, in DMA, for the visible region (bands 1-6): (a) absorption (—) experimental data, (---) fitted data, (···) individual bands; (b) MCD (—) experimental data, (---) fitted data, (···) A terms, (···) B terms. The vertical lines show the band center positions; the line corresponding to the A term is labeled A.

MCD spectra of high quality over an extremely wide wavelength range.

We take the approach in this paper that spectral envelope deconvolution *can give reliable results* if both the absorption and MCD spectra are fitted with the same, or very similar, band center and bandwidth parameters. It is important to underscore the fact

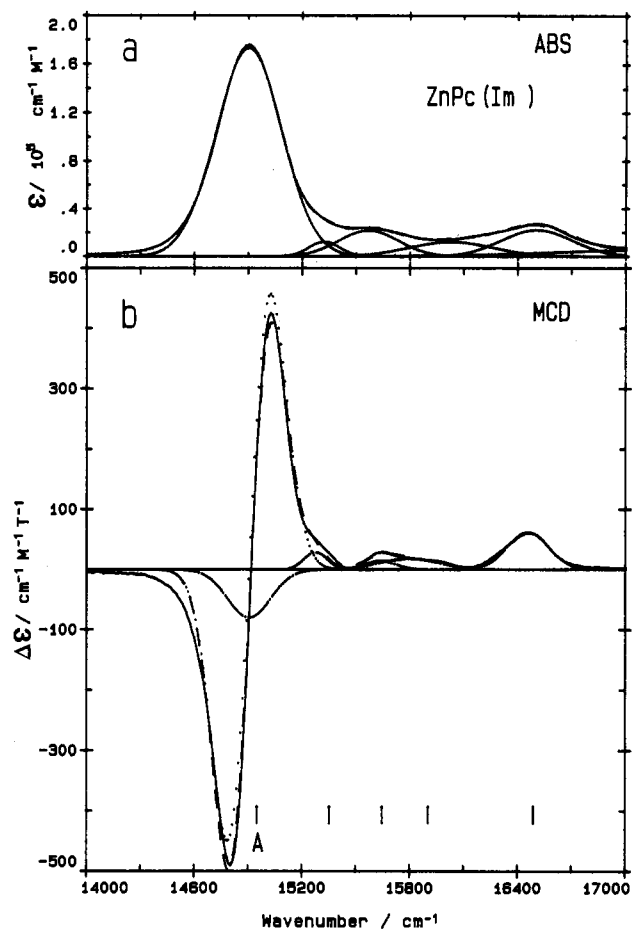


Figure 3. Band analysis for ZnPc(-2)(Im), dissolved in methylene chloride containing 0.05 M tetraethylammonium perchlorate, for the visible region (bands 1-6): (a) absorption (—) experimental data, (---) fitted data, (···) individual bands; (b) MCD (—) experimental data, (---) fitted data (···) A terms, (···) B terms. The vertical lines show the band center positions; the line corresponding to the A term is labeled A.

that, in this work, both sets of spectra (that is, the associated absorption and MCD spectra recorded from the same solution) were fitted with the same set of bands. Removal of only one of the fitted bands resulted in fits that *clearly did not realistically account for all the intensity* in one or the other of the two spectral envelopes. Whenever an A term was used, a B term was also added in. This B term had exactly the same parameters as the A term. If this "straightjacket" on the fitting program were relaxed, then much better fits could be obtained, but the fits to the absorption and MCD spectra were then not related properly and the parameters so calculated clearly would have no physical significance.

The first five singlet excited states in unoxidized phthalocyanine complexes have been described by Gouterman and co-workers^{12,19} as Q, B, N, L, and C, ranging in energy from 15 000 to about 42 000 cm⁻¹. The one-electron transitions assigned to the first four of these states are shown in Figure 1. With the high symmetry of the π ring, each of these transitions will be degenerate and A terms are to be expected in the MCD spectrum.^{12,19,25,36,40} Identification of these degenerate transitions within the MCD spectrum provides a useful tool for locking the experimental data to the state picture calculated theoretically. In spectra of the π-cation species, we anticipate that new transitions, assigned as π → π*, which originate from filled e_g and a_{2g} (π) orbitals lying below the partially filled a_{1u} HOMO, will be observed throughout the visible-UV region. These bands will overlay the Q-C set, which will still provide much of the intensity observed in both absorption and MCD spectra.²⁰

I. Spectral Data. Figures 2 and 3 show (as the solid lines) the absorption and MCD spectra for ZnPc(CN⁻) and ZnPc(Im),

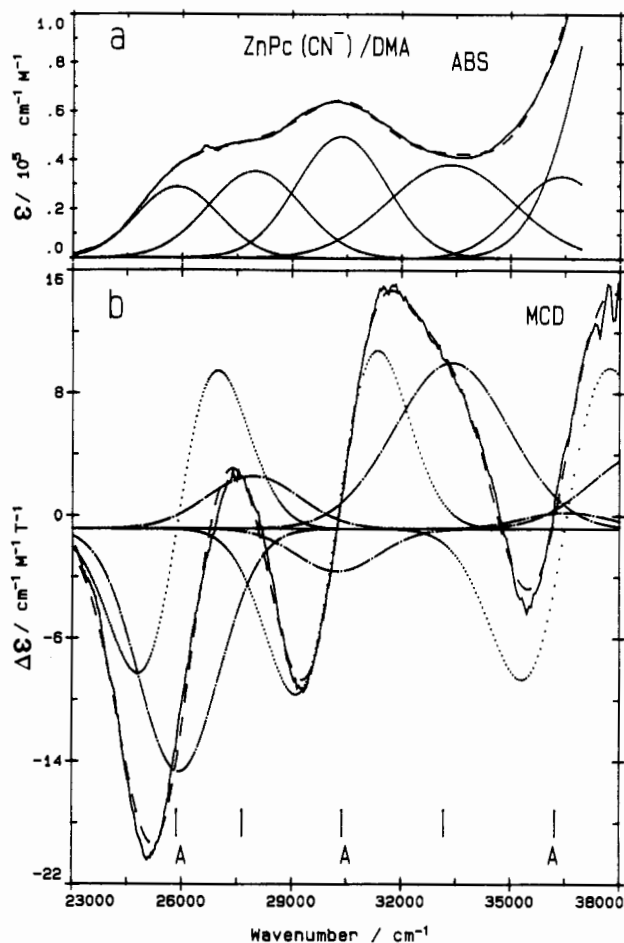


Figure 4. Band analysis for ZnPc(-2) with added CN⁻ ligand, in DMA, for the ultraviolet region (bands 7–12): (a) absorption (—) experimental data, (---) fitted data, (···) individual bands; (b) MCD (—) experimental data, (---) fitted data, (···) *A* terms, (···) *B* terms. The vertical lines show the band center positions; the lines corresponding to the *A* terms are labeled *A*.

respectively, in the Q-band region. The MCD spectra indicate that the Q band near 15 000 cm⁻¹ (670 nm) is degenerate. The vibrational overtone bands between 15 200 and 17 500 cm⁻¹ are a typical feature of MPc complexes; deconvolution always indicates a series of weak, positive *B* terms, unlike the case for the more pronounced bands observed for porphyrins.¹² The spectral region between 20 000 cm⁻¹ (500 nm) and 40 000 cm⁻¹ (250 nm) is much more complicated, even for complexes in which no charge transfer is to be expected between the metal and the π ring. Figures 4 and 5 show the absorption and MCD spectra for these same complexes in the B-band region. In both cases, in the absorption spectrum, a very poorly resolved set of bands leads to a rising, intense absorption above 42 000 cm⁻¹. The MCD spectra reveal far more detail, but the effect of the overlapping bands makes the determination of the energies of individual bands impossible without full spectral envelope deconvolution. The differences between the cyanide (Figure 3) and imidazole (Figure 5) spectra have been noted previously^{28,29,43} and relate to axial ligand effects.

Figures 6 and 7 show the absorption and MCD spectra (solid lines) for the one-electron, ring-oxidized [ZnPc(-1)(Im)]^{•+} complex. As before, for the unoxidized complexes, it is the MCD data that best indicate the large number of individual transitions that are responsible for the observed intensity. The spectrum of the radical cation spans a much wider wavelength range than does the spectrum of the neutral complex. The spectrum in the visible–near-IR region (Figure 6) loses the simplicity of that for the neutral ZnPc. In addition, a new band is found in the characteristic window in the 20 000-cm⁻¹ (500-nm) region observed for

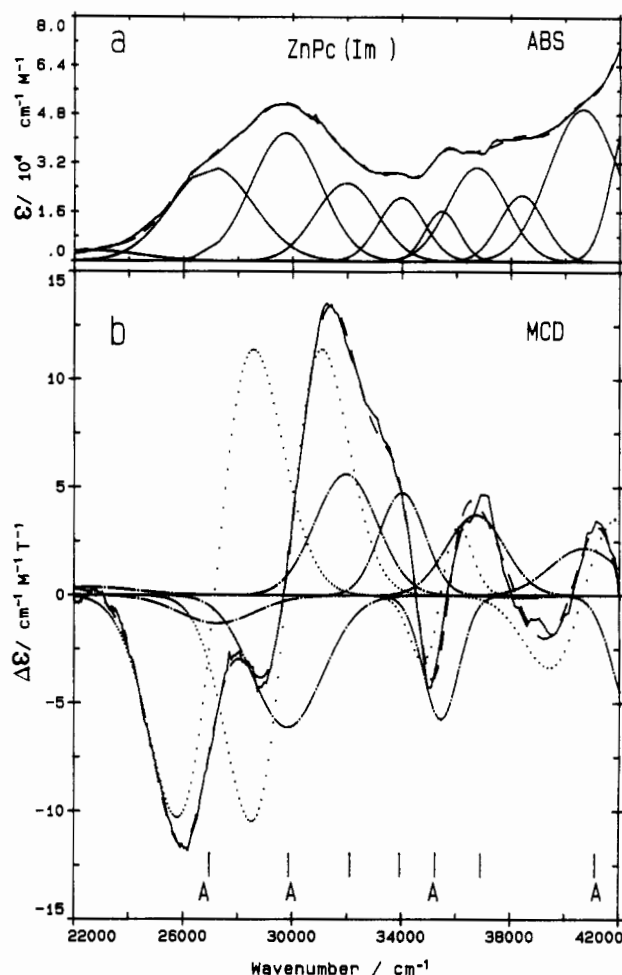


Figure 5. Band analysis for ZnPc(-2)(Im), dissolved in methylene chloride containing 0.05 M tetraethylammonium perchlorate, for the ultraviolet region (bands 7–16): (a) absorption (—) experimental data, (---) fitted data, (···) individual bands; (b) MCD (—) experimental data, (---) fitted data, (···) *A* terms, (···) *B* terms. The vertical lines show the band center positions; the lines corresponding to the *A* terms are labeled *A*.

many phthalocyanine complexes. Between 18 000 and 39 000 cm⁻¹ there is a series of overlapping bands that results in considerable complexity in both the absorption and MCD spectra. Low-temperature (4.2 K) MCD spectra measured for ZnPc(-1) showed no temperature dependence at all.⁴⁸ EPR spectra recorded at 78 K exhibited an intense, organic-radical-like spectrum, with a derivative signal centered on $g = 2.0055$ having a width of 3.8 G.¹⁸ These results indicate that the ground state of the ZnPc(-1) species is essentially orbitally nondegenerate with little spin–orbit coupling induced by the central zinc atom. Thus, the observed MCD spectra at room temperature are dominated by a mixture of *A* and *B* terms, rather than *C* terms.

II. Spectroscopic Analysis. In this section, we use the deconvolution data to characterize the absorption spectra in terms of the number of bands, and the energies and degeneracies of the transitions responsible for the observed intensity. The results of these calculations are plotted on an energy scale (Figure 8) for comparison with the predicted state energies. Despite problems with the choice of band-shape function that might be used, fitting the observed spectral envelope with a set of Gaussian or Gaussian-like bands is the best method for obtaining a set of parameters that describe the number and energy of the transitions present. Plots of residuals showed no systematic errors that would suggest that the choice of band shape was a problem. The combination of bands that can be used to fill either the MCD or the absorption spectral envelopes can vary tremendously from calculation to calculation, depending on the constraints used. In order to reduce this ambiguity, we have fitted the absorption and MCD spectra

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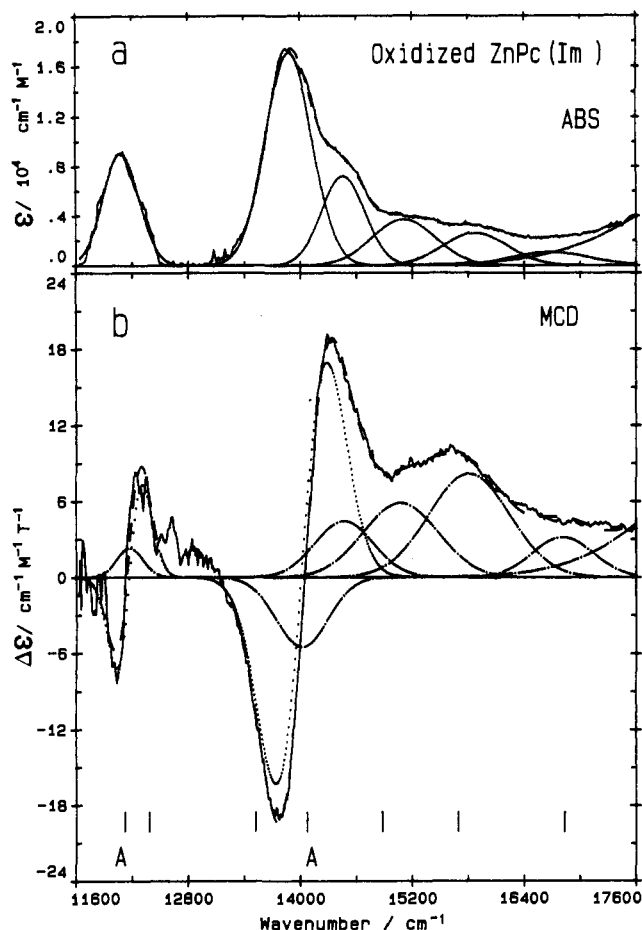


Figure 6. Band analysis for ZnPc(-1)(Im), dissolved in methylene chloride containing 0.05 M tetraethylammonium perchlorate, for the visible region (bands 1-6): (a) absorption (—) experimental data, (---) fitted data, (· · ·) individual bands; (b) MCD (—) experimental data, (---) fitted data, (· · ·) *A* terms, (- · -) *B* terms. The vertical lines show the band center positions; the lines corresponding to the *A* terms are labeled *A*.

with exactly the same number of bands, using very similar band widths and band centers. This technique greatly improves the quality of the resultant parameters as long as each transition gives rise to intensity in both the absorption and MCD spectra.

The few reports of other such calculations for the spectra of MPc complexes include the deconvolution of absorption and MCD spectra of a range of MPc α -phase thin films²⁴ and the deconvolution of the solution absorption spectra of a variety of MPc complexes.⁴³ The previous band-fitting calculations of Stillman for ZnPc in solution⁴³ were carried out solely on the absorption spectra of the ZnPc(Me₂SO) and ZnPc(CN⁻) complexes. The results of these calculations indicated that two bands were required to fill the absorption envelope in the Soret-band region; for ZnPc(CN⁻) the two bands were centered at 25 263 and at 29 922 cm⁻¹. In the ZnPc(CN⁻) MCD spectrum, it was clear that an *A* term was present under each of these bands. Only a single *A* term was observed for the ZnPc(Me₂SO) complex. Because these fitting calculations were only based on the absorption spectra, it was not possible to determine whether the two bands observed for ZnPc(CN⁻) had coalesced in the ZnPc(Me₂SO) spectra or whether the second MCD band was a new band, perhaps of charge-transfer origin involving the ring and the cyanide. In our present study, we have reinvestigated the absorption and MCD spectra of the neutral ZnPc(L) complexes.

We analyzed the MCD and absorption spectra in two ways. The method of moments^{27,44} was used to extract magnetic moment values (from the *A/D* ratio)^{28,29,36} directly by integration, in the

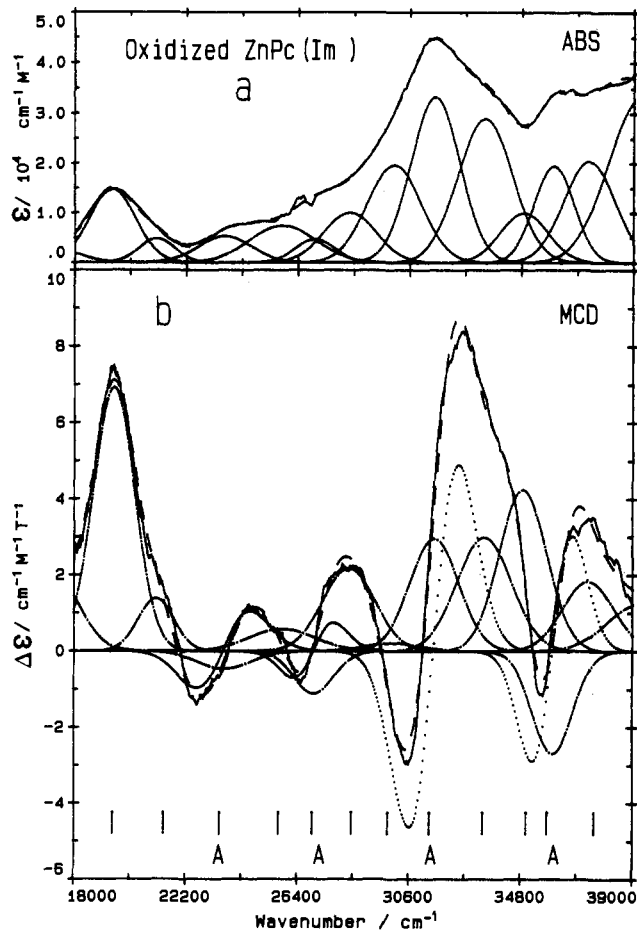


Figure 7. Band analysis for ZnPc(-1)(Im), dissolved in methylene chloride containing 0.05 M tetraethylammonium perchlorate, for the ultraviolet region (bands 7-19): (a) absorption (—) experimental data, (---) fitted data, (· · ·) individual bands; (b) MCD (—) experimental data, (---) fitted data, (· · ·) *A* terms, (- · -) *B* terms. The vertical lines show the band center positions; the lines corresponding to the *A* terms are labeled *A*.

well-resolved Q-band region. The number of transitions that were responsible for the observed spectral intensity throughout the 220-900-nm range was estimated by using band-shape fitting. As an aid in the comparison of magnetic moment values calculated by each method, we also carried out a band-fitting calculation in the Q-band region. This comparison is useful in estimating the extent of errors that might be expected in the *A/D* values derived from the deconvolution calculations.

(i) Analysis of the Q Band of ZnPc(L) Complexes. The Q-band-region MCD envelope for ZnPc, dissolved in DMA containing excess CN⁻ ligand (Figure 2 and Table I, bands 1-6), and for ZnPc(Im), dissolved in methylene chloride containing 0.05 M [Et₄N]ClO₄ (Figure 4 and Table II, bands 1-6), can be filled with a positive *A* term and a series of *B* terms. The results of the moment analysis of the MCD and absorption spectra of the Q band of the ZnPc species are summarized in Table III. We note that the values shown in Table III follow the new definitions of Piepho and Schatz,²⁷ so that these numbers cannot be compared directly with those of previous work,²⁸ where the *A/D* values were calculated in a different manner from Stephens' earlier definitions.^{44,45} It is, therefore, more useful to compare the values of the moments themselves, i.e. $\langle \Delta \epsilon_M \rangle_0$, $\langle \Delta \epsilon_M \rangle_1$, or the normalized ratio $\langle \Delta \epsilon_M \rangle_1 / \langle \epsilon \rangle_0$. The value of the magnetic moment for the phthalocyanine Q- and B-band excited states has been shown³⁶ to be twice the $(A_1/D_0)\mu_B$ value.

In general, as shown in Table III, the value of the Q-band angular momentum for a range of ZnPc species is approximately

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Table I. Band-Fitting Parameters^a for ZnPc(-2) with Added CN⁻ Ligand, in DMA

band no.	ν , cm ⁻¹	λ , nm	$\Delta\nu$, cm ⁻¹	D_0 , ^b D ²	band type	$\langle\Delta\epsilon_M\rangle_n$ ^c	$10^3 A_1$, D ² ; $10^3 B_0$, D ² cm ^d	$10^3(B_0/D_0)$, cm	A_1/D_0	μ , ^e μ_B
1	14951	669	257	25.6	A	6541	42890		1.67	1.57
					B	-6.8	-44.3	-1.73		
2	15353	651	200	1.1	B	2.10	13.8	12.5		
3	15648	639	170	2.0	B	1.00	6.6	3.30		
4	15903	629	326	1.8	B	1.96	12.8	7.11		
5	16489	606	250	3.9	B	4.31	28.2	7.23		
6	17571	569	1935	1.5	B	1.77	11.6	7.73		
7	25874	386	2573	9.7	A	1785	11710		1.21	1.13
					B	-1.59	-10.4	-1.07		
8	27897	358	2954	12.4	B	0.36	2.39	0.19		
9	20213	331	2645	15.5	A	1839	12060		0.78	0.73
					B	-0.25	-1.61	0.02		
10	33322	300	3709	15.1	B	1.22	7.98	0.10		
11	36505	274	2842	8.8	A	1594	10450		1.19	1.11
					B	-0.08	0.06	-0.007		
12	38750	258	3636	55.9	B	0.48	3.17	0.06		

^aStatistics: B-band region, $\lambda = 230\text{--}500$ nm, $\chi^2 = 0.30$, $\sum(\Delta\epsilon)^2 = 21.2$; Q-band region, $\lambda = 500\text{--}800$ nm, $\chi^2 = 28.8$, $\sum(\Delta\epsilon)^2 = 64304$. ^b D_0 (dipole strength) = $\langle\epsilon\rangle_0/326.6$; see ref 27, p 537. ^c $\langle\Delta\epsilon_M\rangle_1$ is the first moment and $\langle\Delta\epsilon_M\rangle_0$ is the zeroth moment of the MDC. When fitting with an A term, the program calculates $\langle\Delta\epsilon_M\rangle_1$; therefore, $n = 1$ in the table. When fitting with a B term, the program calculates $\langle\Delta\epsilon_M\rangle_0$; therefore $n = 0$ in the table. The Faraday term values, A_1 and B_0 , are calculated directly from the moments as follows: $A_1 = \langle\epsilon_M\rangle_1/152.5$ and $B_0 = \langle\epsilon_M\rangle_0/152.5$. ^dSee ref 27, p 537. A_1 data is printed above B_0 data when both an A and B term are used. ^e $\mu =$ magnetic moment, calculated as $2((A_1/D_0)0.4669)$.

Table II. Band-Fitting Parameters^a for ZnPc(-2)(Im) Dissolved in Methylene Chloride Containing 0.05 M Tetraethylammonium Perchlorate

band no.	ν , cm ⁻¹	λ , nm	$\Delta\nu$, cm ⁻¹	D_0 , ^b D ²	band type	$\langle\Delta\epsilon_M\rangle_n$ ^c	$10^3 A_1$, D ² ; $10^3 B_0$, D ³ cm ^d	$10^4(B_0/D_0)$, cm	A_1/D_0	μ , ^e μ_B
1	14906	671	281	16.1	A	1795	11770		0.73	0.68
					B	-1.61	-10.54	-0.65		
2	15276	655	150	0.50	B	0.30	1.98	3.96		
3	15638	640	200	1.7	B	0.19	1.28	0.75		
4	15794	633	400	1.3	B	0.48	3.18	2.45		
5	16458	608	271	2.0	B	1.09	7.17	3.58		
6	17674	566	2159	1.4	B	0.05	0.35	0.25		
7	22495	445	3912	2.1	B	0.07	0.45	0.21		
8	27513	368	3272	13.0	A	3181	20860		1.60	1.50
					B	-0.17	-1.09	-0.08		
9	29778	336	3016	13.7	A	2488	16320		1.19	1.11
					B	-0.66	-4.32	-0.65		
10	31933	313	2683	6.9	B	0.50	3.29	0.48		
11	34008	294	1959	3.9	B	0.29	1.92	0.49		
12	35437	282	1535	2.2	A	155.0	1016		0.46	0.43
					B	-0.26	-1.74	-5.28		
13	36689	273	2506	6.9	B	-0.27	1.78	0.79		
14	38362	261	1823	3.6	B	-0.005	-0.04	-0.01		
15	40655	246	2946	12.0	A	549.4	3603		0.30	0.60
					B	0.17	1.11	0.09		
16	42511	235	1729	6.9	B	-0.25	-1.63	0.24		

^aStatistics: $\lambda = 230\text{--}500$ nm, $\chi^2 = 0.54$, $\sum(\Delta\epsilon)^2 = 77.6$; $\lambda = 500\text{--}800$ nm, $\chi^2 = 0.70$, $\sum(\Delta\epsilon)^2 = 56.9$. ^{b-e}Refer to respective footnotes in Table I.

Table III. Moment Analysis of the Q-Band Absorption and MCD Spectra of ZnPc(L) Complexes

L ^a	ν , cm ⁻¹	D_0 , ^b D ²	$\langle\Delta\epsilon_M\rangle_1$	A_1 , ^d D ²	A_1/D_0	μ , ^e μ_B	$\langle\Delta\epsilon_M\rangle_0$	$10^3 B_0$, D ² cm ^d	$10^4(B_0/D_0)$, cm
Im	15289	23.8	5469	35.8	1.51	1.40	1.01	6.63	2.79
py	15280	31.2	12410	81.6	2.62	2.45	1.19	7.79	2.50
CN ⁻	15252	36.4	19770	129.0	3.55	3.32	3.73	2.44	6.70

^aZnPc(Im) was dissolved in methylene chloride containing 0.05 M [Et₄N]ClO₄, ZnPc(CN⁻) was dissolved in DMA, and ZnPc(py) was dissolved in methylene chloride. ^{b,d,e}Refer to respective footnotes in Table I.

the same as has previously been determined,^{28,29,43} the differences being primarily due to ligand effects. Our present values range from 1.4 μ_B ($\mu_B =$ Bohr magneton) for ZnPc(Im) to 3.32 μ_B for ZnPc(CN⁻) dissolved in methylene chloride. Comparison between the magnetic moment obtained by the moment analysis (Table III) and the value obtained from the fitting procedures (Tables I and II) shows that the fitting procedures underestimate the value of the magnetic moment. However, when the moment calculation is carried out over just the A-term part of the band, not including the vibronic region, the values for $\langle\Delta\epsilon_M\rangle_1$ drop (for Im, $\langle\Delta\epsilon_M\rangle_1 = 2120$; for py, $\langle\Delta\epsilon_M\rangle_1 = 4990$; for CN⁻, $\langle\Delta\epsilon_M\rangle_1 = 7850$), so that they now match quite closely the values obtained from the fitting (Tables I and II). This means that the absolute value of magnetic moment obtained from fitting probably always underestimates

the actual value because the whole transition is not included.

We interpret the span in magnetic moment values for the Q band in terms of the effect of the axial ligation of the zinc in the following manner. It has been proposed³⁶ that the value of the angular momentum of the metal phthalocyanine will always be less than the angular momentum of the pure phthalocyanine (Pc(-2)) ring, since the empty $1e_g(\pi^*)$ orbitals of the phthalocyanine can interact with the metal orbitals, thus reducing the value of the angular momentum. As Table III shows, the angular momentum of the ZnPc species follows the trend ZnPc(CN⁻) > ZnPc(py) > ZnPc(Im). We explain the order in this series as the effects of π -acceptor and σ -donor strengths of the axial ligand on the π ring MO's. The CN⁻ ion is a good π acceptor, and when it is placed on the axial position above the metal ion, CN⁻ can

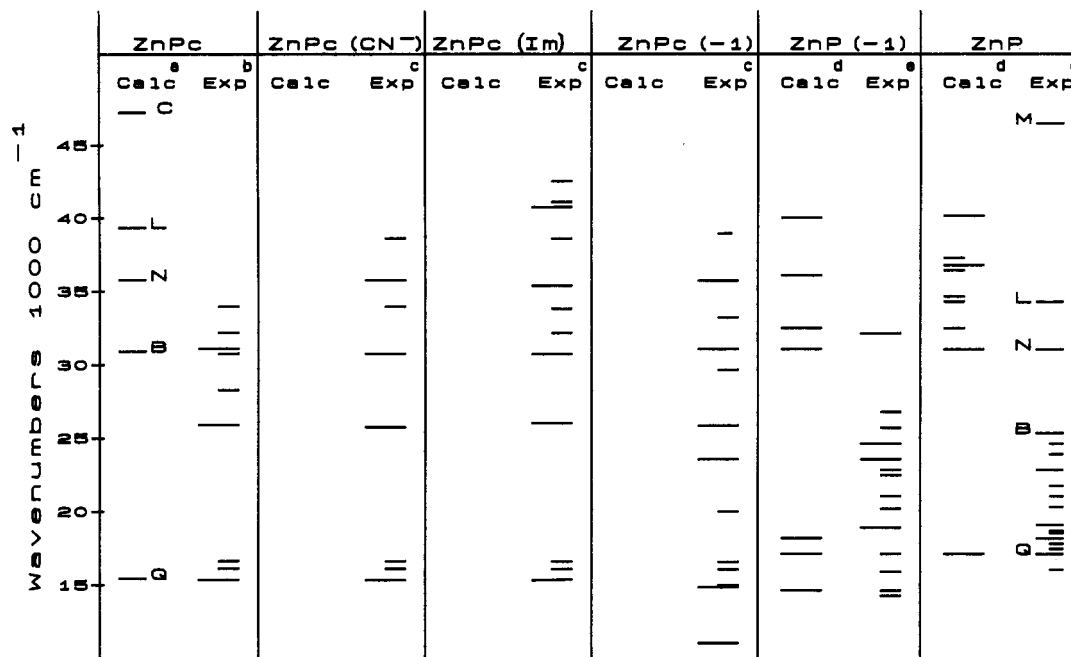


Figure 8. Comparison between the energies of the transitions calculated from the spectra of the oxidized and neutral ZnPc species. The long lines represent energies of the degenerate transitions while the short lines represent the energies of the nondegenerate transitions. Data for the plot were obtained from the following sources: (a) ref 19; (b) ref 43; (c) this work; (d) ref 26; (e) ref 46.

Table IV. Band-Fitting Parameters^a of ZnPc(-1)(Im) Dissolved in Methylene Chloride Containing 0.05 M Tetraethylammonium Perchlorate

band no.	ν , cm^{-1}	λ , nm	$\Delta\nu$, cm^{-1}	D_0 , ^b D^2	band type	$\langle\Delta\epsilon_M\rangle_n^c$	$10^3 A_1, D^2$; $10^3 B_0, D^2 \text{ cm}^d$	$10^4(B_0/D_0)$, cm	A_1/D_0	$\mu_s^e \mu_B$
1	12170	822	329	1.09	A	47.8	313.5		0.29	0.27
					B	0.07	0.44	0.40		
2	14008	714	650	2.34	A	372.7	2444		1.04	0.96
					B	-0.27	-1.78	-0.76		
3	14461	691	734	0.86	B	0.24	1.58	1.84		
4	15062	664	940	0.63	B	0.39	2.55	4.04		
5	15800	633	1018	0.43	B	0.56	3.68	8.56		
6	16805	595	766	0.20	B	0.15	1.01	5.05		
7	19554	511	2759	7.9	B	2.87	18.80	2.37		
8	21065	475	1585	1.11	B	0.11	0.72	0.61		
9	23602	424	2356	1.72	A	175.4	1150		0.67	0.62
					B	-0.05	-0.32	-0.19		
10	25745	388	2913	2.70	B	0.07	0.46	0.17		
11	26999	370	1763	1.00	A	61.8	405.0		0.41	0.38
					B	-0.08	-0.51	-5.10		
12	28304	353	2323	2.66	B	0.19	1.24	0.47		
13	29969	334	2394	5.14	B	0.08	0.12	0.02		
14	31521	317	2168	7.42	A	529.3	3471		0.47	0.44
					B	0.22	1.42	1.91		
15	33393	295	2419	6.83	B	0.23	1.51	0.22		
16	34860	287	2097	1.94	B	0.27	1.78	0.92		
17	35990	278	1767	3.09	A	191.2	1254.0		0.41	0.38
					B	-0.14	-0.92	-0.30		
18	37313	268	2274	4.14	B	0.12	0.78	0.19		
19	39238	255	2883	7.70	B	0.097	0.63	0.08		

^aStatistics: B-band region, $\lambda = 230\text{--}500$ nm, $\chi^2 = 0.21$, $\sum(\Delta\epsilon)^2 = 34.13$; Q-band region, $\lambda = 500\text{--}800$ nm, $\chi^2 = 1.16$, $\sum(\Delta\epsilon)^2 = 188.7$. ^{b-c}Refer to respective footnotes in Table I.

pull the electron density away from the metal center, thus lowering the energy of the metal d orbitals and hence decreasing the interaction with the $1e_g(\pi^*)$ orbital of the phthalocyanine. This results in an increase in the angular momentum. Imidazole, however, is a strong σ donor, and its interaction with the metal results in an increase of electron charge on the metal, thus increasing the energy of the metal d orbitals and, hence, increasing the interaction with the $1e_g(\pi^*)$ orbital of the phthalocyanine. The effect is that the angular momentum is reduced. Pyridine is a weaker σ donor than imidazole,³⁷ and hence ZnPc(py) will have an angular momentum intermediate between those of ZnPc(Im) and ZnPc(CN⁻), as observed.

(ii) **Deconvolution of the Soret-Band Region of ZnPc(L) Complexes.** Figure 3 and Table I (bands 7–12) show the results

of the analysis for the MCD and absorption components in the Soret region of the spectra of ZnPc(CN⁻) in DMA. Using the absorption–MCD combination technique, we were able to calculate, with little ambiguity, that five separate bands were required to fill the absorption envelope. The MCD analysis required three positive A terms, at 25874 cm^{-1} (band 7), 30213 cm^{-1} (band 9), and 36505 cm^{-1} . For degenerate transitions, both an A term and a B term were used in the fitting. Three separate B terms are required in the fit. With the linked absorption and MCD fitting procedure, the fits obtained are not always of the precision that the program is capable of achieving if left unconstrained. There is some sacrifice in rms values. The MCD spectrum of ZnPc(Im) in methylene chloride containing 0.05 M tetraethylammonium perchlorate (Figure 5 and Table II, bands 7–16) again shows the

presence of three degenerate transitions, identified by *A* terms, at 27 513, 29 778, and 35 437 cm^{-1} . In addition, because of the transparent nature of methylene chloride in the ultraviolet region when compared to the behavior of DMA (the spectrum extends to higher energies, $>42\,000\ \text{cm}^{-1}$), another degenerate transition at 40 655 cm^{-1} (band 15) is evident.

(iii) **Comparison between Experimentally Determined and Theoretically Calculated Band Centers: Unoxidized ZnPc.** Figure 8 compares the energies of the bands obtained in this work with the theoretically calculated energies reported by Gouterman et al.¹⁹ and with data reported elsewhere⁴⁶ for the spectra of zinc porphyrins (ZnP).

Our approach in the analysis of the absorption spectrum is to use the MCD data to identify the main degenerate transitions from the characteristic *A* terms. The four states shown in Figure 1 are each degenerate. Because the ZnPc data should contain no charge-transfer bands, we can simply choose the first four degenerate transitions from the MCD spectrum. In the spectra of the cyanide and imidazole complexes, it would have been more usual to associate the band near 30 000 cm^{-1} (band 9) with the B band ($1a_{2u}(\pi) \rightarrow 1e_g(\pi^*)$) of the Gouterman model.¹⁹ However, we clearly observe positive *A* terms to lower energy in each of the ZnPc(L) complexes we have examined, which strongly argues that this lower energy band is the B band. Comparison between the B-band energies of the ZnPc and ZnP systems (Figure 8) also suggests that perhaps the lower energy band, which is most clearly seen in the MCD spectrum of ZnPc(CN⁻) as band 7, is the B band of the phthalocyanines. Thus, the band near 30 000 cm^{-1} should be associated with either the N band ($2a_{2u}(\pi) \rightarrow 1e_g(\pi^*)$, Figure 1) or a second B-band component that arises from the very complicated mixture of atomic orbitals used in the calculations of the states that arise at this energy. In the absence of the CN⁻ ligand the lower energy band coalesces with the main envelope (Figure 5); however, the band analysis still requires the presence of two *A* terms in the Soret-region band envelope in order to obtain a proper fit, even though the bands are not completely resolved in either the MCD or the absorption spectrum. At higher energies (35 437 cm^{-1} , band 12, for ZnPc(Im)), another *A* term is observed, which we associate with the L band ($1a_{1u}(\pi) \rightarrow 2e_g(\pi^*)$). With the UV-transparent methylene chloride solvent, we observe a rather poorly resolved band at 40 655 cm^{-1} , which we associate with the C band.

Thus, using the data that span a wide wavelength range obtained for ZnPc(Im) in CH₂Cl₂ (Table II), we locate the Q band at 14 906 cm^{-1} , the B band at 27 513 cm^{-1} , the N band at 29 778 cm^{-1} , the L band at 35 437 cm^{-1} , and the C band at 40 655 cm^{-1} . There is some "wobble" in the energies of these bands when the ZnPc(CN⁻) data is used (Table I), which is related to the axial ligand effects of cyanide and imidazole coordination. It is clear that in order to assign the spectrum of a phthalocyanine complex, the MCD spectrum has to be known. It is not possible to deconvolute the absorption spectrum in the Soret band region on its own and then simply lay the positions of these states on to the theoretically calculated state picture.

(iv) **Deconvolution of the Spectra of the Oxidized Complex [ZnPc(-1)]⁺.** We have chosen the spectra of [ZnPc(-1)(Im)]⁺ as the example to use for the full deconvolution calculation. Figures 6 and 7 show the absorption spectra spread out into two regions: Figure 6 covers the Q-band region, 11 000 cm^{-1} (900 nm) to 17 600 cm^{-1} (570 nm), while Figure 7 covers the Soret-band region, 17 000 cm^{-1} (590 nm) to 39 000 cm^{-1} (255 nm). Clearly, there are a large number of bands, especially in the 250–400-nm region. We use a remarkable sum of 19 bands to fill most of the intensity in both the absorption and MCD spectra. However, by linking the absorption parameters with the MCD parameters, we do, as before, believe that this is a reasonably unambiguous fit. We feel that it is important to point out that we could not identify individual bands from these spectra without using the computer deconvolution techniques; the spectra are just too complicated.

There are a number of striking features: (i) each of the many bands in the absorption spectrum matches a distinct feature in the MCD spectrum; (ii) the 12 170- cm^{-1} (822-nm) transition is degenerate, as is the 14 008- cm^{-1} (714-nm) band; (iii) the transition responsible for the broad absorption near 500 nm (19 554 cm^{-1}) is nondegenerate; (iv) two well-defined *A* terms identify degenerate transitions in the Soret region at 31 521 cm^{-1} (317 nm) and 35 990 cm^{-1} (278 nm); (v) each of the *A* terms is of the same, positive sign, with angular momentum values being significantly quenched when compared with those of the unoxidized species.

(v) **Comparison between Experimentally Determined and Theoretically Calculated Band Centers for [ZnPc(-1)]⁺.** Because there are so few data in the literature for π -cation-radical species of other metallophthalocyanines, it is difficult to compare spectra quantitatively. Our [ZnPc(-1)]⁺ absorption data are similar to data reported for the π -cation-radical species of RuPc¹⁴ and CoPc and FePc.⁴⁷ The MCD data for [ZnPc(-1)]⁺ resemble data that we have previously observed with [RuPc(-1)]⁺.¹⁴ Absorption data recorded transiently for the oxidation of ZnPc by methylviologen (MV)³ also exhibit this same type of band envelope. The [ZnPc(-1)]⁺ data reported here are generic data that can be used in assigning the spectra of other, more complicated systems. The first task in assigning the spectrum is identifying from this large number of bands those that arise from $\pi \rightarrow \pi^*$ transitions and those that arise from $\pi \rightarrow \pi$ transitions. Because of the similarities in the composition of the band envelopes near 700 nm (see also Figure 8) we identify the band at 14 000 cm^{-1} as the Q band. The band at this energy in many of the complexes that we have studied exhibits the same type of characteristics as the Q band in the unoxidized complex, that is, a positive *A* term, followed at higher energy by a series of overlapping, weak, positive *B* terms that arise from the vibronic transitions.

Although theoretical calculations on the electronic transitions for a number of neutral metallophthalocyanines and porphyrins are available,^{19,39} the first attempts to interpret the phthalocyanine and porphyrin π -cation-radical absorption spectra have been presented only very recently by Minor, Gouterman, and Lever for phthalocyanines²⁰ and by Edwards and Zerner for the porphyrins.²⁶ Because of the very large differences between the spectra of the two known types of π -cation-radical species^{14,16,17,46} we will compare our experimental results only with the theoretical treatment of Minor et al.²⁰

Minor and co-workers have reported spectral data for the cationic and anionic complexes of a wide range of phthalocyanines.²⁰ However, many of the sets of data reported for the π -cation-radical species, the MPc(-1)L complexes, were obtained from samples in the solid state, including the data for ZnPc(-1).⁴¹ We believe that the use of the solid-state spectra complicates the assignment problem considerably because of the Davydov coupling. In addition, no information concerning transition degeneracies was used, so the assignments were made on the basis of energy alone. As can be seen in Figures 6 and 7, there are a large number of transitions observed between 10 000 and 40 000 cm^{-1} , far more than the five reported by Myers et al.⁴¹ from the solid-state data.

We identify which transition should be associated with which particular excited state by using as a guide the degeneracies introduced in fitting the MCD data. One-electron oxidation should not affect the degeneracies of the π states. We expect the $\pi\pi^*$ states named Q, B, N, L, and C each to have ²E_g symmetry, and transitions from the ²A_{1u} ground state should result in *A* terms being observed in the MCD spectrum of [ZnPc(-1)]⁺, just as in neutral ZnPc. The energies of degenerate transitions are drawn on Figure 8 as long bars, for ZnPc(-1)(Im).

Clearly, the degenerate transitions observed in the spectra of the [ZnPc(-1)]⁺ species near 14 000, 27 000, 31 500, and 36 000 cm^{-1} line up too closely with the Q, B, N, and L bands, respectively, of the neutral complex for these bands not to be those same transitions. That leaves significant intensity near 12 200, 19 500,

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(47) Nyokong, T.; Gasyna, Z.; Stillman, M. J. *ACS Symp. Ser.* **1986**, No. 321, 309–327.

(48) Gasyna, Z.; Nyokong, T.; Stillman, M. J., unpublished data.

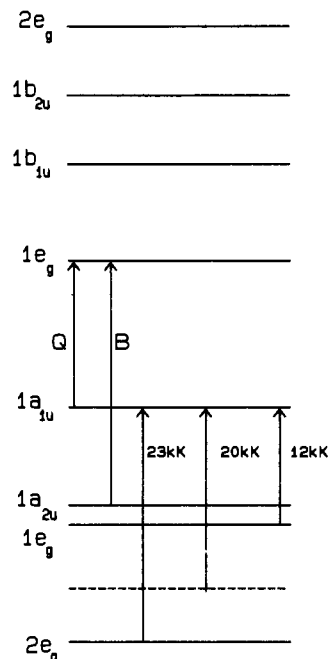


Figure 9. The molecular orbitals for $[\text{ZnPc}(-1)]^{2+}$ that result in absorption between 10 000 and 45 000 cm^{-1} . The order of the orbitals is taken from the results of fitting to the spectra of $\text{ZnPc}(-1)(\text{Im})$.

and 23 600 cm^{-1} unaccounted for. We assign each of these bands to $\pi \rightarrow \pi$ transitions, from low-lying π MO's into the a_{1u} HOMO. The 12 200- and 23 600- cm^{-1} transitions are degenerate; the 19 500- cm^{-1} transition is nondegenerate. Acceptable transitions are as follows: $1e_g(\pi)$ or $2e_g(\pi) \rightarrow a_{1u}(\pi)$ for degenerate excited states, which should result in a Faraday A term, and $a_{2g}(\pi) \rightarrow a_{1u}(\pi)$, for nondegenerate excited states, which will result in B terms. In Figure 9 we have plotted the available molecular orbitals that represent one-electron transitions into the half-filled a_{1u}

orbital, which we suggest could result in the observed MCD spectral features. Thus, we use the low-lying $1e_g$ and $2e_g$ MO's to account for the 12 170- and 23 602- cm^{-1} bands, respectively. We cannot identify, however, a nondegenerate transition to account for the 19 54- cm^{-1} band.

Conclusions

Spectral envelope deconvolution calculations can provide unambiguous data on the location and polarizations of many of the individual bands observed in spectra as complicated as those recorded for both unoxidized and oxidized metallophthalocyanines. The essential feature in these calculations is the availability of MCD data. The calculations indicate that, for complexes of ZnPc , there are five degenerate transitions, at approximately 14 900, 27 500, 29 800, 35 400, and 40 600 cm^{-1} ; these transitions are associated with the Q, B, N, L, and C transitions of the Gouterman four-orbital model.

Despite extensive overlap of bands in the spectra of the oxidized $[\text{ZnPc}(-1)]^{2+}$ species, the deconvolution calculations clearly indicated that a similar set of bands exists. It is suggested that the Q band is located at 14 000 cm^{-1} , with the B, N, and L bands located at 27 000, 31 500, and 36 000 cm^{-1} , respectively. Thus the Q-band energy is lower, and each of the other bands blue shifts. Bands at approximately 12 000, 19 500, and 23 600 cm^{-1} are identified as $\pi \rightarrow \pi$, into the a_{1u} HOMO. Further detailed, quantitative analyses of the spectra of oxidized phthalocyanines are needed in order to determine how general this assignment is.

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Effect of Pressure on the Vibrational Spectra of Solids. 5. Raman Spectrum of Zinc Bis(pyridine) Dichloride

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The effect of pressure on the Raman spectrum of $\text{ZnCl}_2(\text{py})_2$, extenuating over the range of the internal modes of the pyridine ligand was studied. The internal vibrational modes of pyridine coordinated to the zinc tetrahedrally did not show any major differences from the vibrations of solid pyridine at low pressures. Above 10 kbar, a phase transition occurs involving changes in the C-H stretch and in-plane H-bend and out-of-plane H-bend vibrations of the ligand. The lattice region for $\text{ZnCl}_2(\text{py})_2$ in this higher pressure phase also differs substantially from that found for this compound in the low-pressure phase, but the Raman results show that a polymeric octahedral structure is not formed. The spectral changes are explained in terms of a rotation about the Zn-N bond, which affects the Cl-H nonbonded interactions.

Introduction

Numerous vibrational studies have been carried out on complexes of the type MX_2L_2 (X = halide, L = pyridine or substituted pyridine) in an effort to assign the bands occurring in the lattice region.¹⁻⁴ Structures found include tetrahedral, square-planar,

polymeric octahedral, distorted tetrahedral, and distorted polymeric octahedral ones.

One of these studies¹ found that the M-X stretching vibrations can give a good indication of the molecular symmetry present in the metal complex. The first-row transition elements of groups VIIa-IIb⁵⁻¹⁰ (groups 7-12¹¹) and Cd(II) and Hg(II)^{9,10,12} all have

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