tonation constant) of the mono(Schiff base) is 7.50, so that the presence of the proton on the phenoxyl anion, hydrogen bonded to the nitrogen (imine), helps to stabilize the Schiff base. In a similar manner the bis(Schiff base) forms both mono- and diprotonated forms with successive log (protonation constant) values of 11.23 and 8.41. A third protonation reaction is half-completed at p[H] 3.17.

The anaerobic cobalt(II) coordination chemistry of this Schiff base is rather simple, in that only two species are formed: a normal complex and a singly protonated complex of the fully formed Schiff base. The log (stability constant) of the 2:1 deprotonated Schiff base and Co(II) is 14.91, while the protonation reaction is characterized by a log (protonation constant) of 6.94. While the normal complex may have a simple planar structure, the monoprotonated complex can be assumed to be protonated at the phenol oxygen on the other fluorosalicylidene moiety, as is the case for protonation of the metal-free Schiff base.

The oxygenation constant determined is much lower than that of CoSALEN. The log (stability constant) is only 38.68, in accordance with the much lower basicity of the ligand. The main difference is in the apparent differences at high p[H] of dioxygen complexes of **4** and **5**. However, the specific mono- and dihydroxylation reactions of the FSALOPHEN Co(II) complex have not been calculated. It is probable, however, that the dioxygen complexes of CoSALEN and Co3FSALOPHEN have similar hydrolytic reactions at high p[H].

Conclusions

While equilibrium potentiometry is used almost routinely to determine the stability constants of metal ions with a variety of basic ligands, this technique has recently been extended in this laboratory to the determination of cobalt(II) Schiff base formation constants of pentadentate ligands and their oxygenation equilibria. The present work goes one step further in showing the method to be applicable to very complicated systems involving Schiff base complex formation and dioxygen equilibria for six components, such as, for example, a phenolic aldehyde, a diamine, a cobalt(II) ion, a substituted pyridine as an auxiliary ligand, dioxygen, and hydrogen ion. The success of this method depends on separate determination of each contributing equilibrium on increasingly complex mixtures, with the final experiment being carried out under oxygen saturation to obtain the oxygenation constant.[17]

Acknowledgment. The work was supported by a cooperative research grant from Dow Chemical Co.

Registry No. OPYDIAMIDE, 115077-75-3; MHBA, 115077-77-5; MBA, 115077-78-6; SALOPYDIAMIDE, 115077-76-4; SALEN, 94-93-9; 3FSALOPHEN, 115077-79-7; O_2, 7782-44-7; dimethyl 2,6-pyridinedicarboxylate, 5453-67-8; 4-picoline, 108-89-4.

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[17] Authors welcome inquiries about the experimental data and the methods employed to convert such data to the equilibrium parameters reported in this paper (409-845-2232).

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Electrochemistry and Spectroscopy of Magnesium Phthalocyanine. Analysis of the Absorption and Magnetic Circular Dichroism Spectra[‡]

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Absorption, magnetic circular dichroism (MCD), and electrochemical properties are reported for a range of magnesium phthalocyanine (MgPc) complexes in methylene chloride and dimethylacetamide solution. The ligands studied include imidazole, methylimidazole, pyridine, 4-methylpyridine, and cyanide. The major effect of the axial ligation on the spectra is to induce a red shift of each of the bands from the positions recorded for MgPc in methylene chloride. Results of reversible cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) of the MgPc complexes are also reported. Representative $E_{1/2}$ values determined for MgPc in dimethylacetamide (DMA) are 1.11 V (formation of the dication), 0.65 V (the monocation), −0.88 V (the monoanion), and −1.43 V (the dianion) vs SCE. Band deconvolution calculations that couple both the absorption and MCD spectra are reported for each of the complexes studied. The energies of the fitted bands are compared with values reported by Gouterman and co-workers[1,2] from theoretical calculations and with experimental results for ZnPc reported by Nyokong et al.[3] The deconvolution analysis located two degenerate transitions in the 330–400-nm region; it is suggested that the B band lies near 360 nm in a typical phthalocyanine complex. Five degenerate electronic transitions were identified in the spectra of the MgPc complexes in methylene chloride solutions through use of the deconvolution calculations. These transitions are centered on 670 nm (14 900 cm^{-1}), 361 nm (27 600 cm^{-1}), 338 nm (29 600 cm^{-1}), 282 nm (35 500 cm^{-1}), and 246 nm (40 500 cm^{-1}) and correspond to the theoretically predicted Q, B, N, L, and C transitions.

Introduction

The spectral and electrochemical properties of the porphyrins and phthalocyanines have been extensively studied as models of heme proteins and chlorophylls.[1-15] The 18-π-electron system of the porphyrins and phthalocyanines, together with the overlap of orbitals from the central metal, allows for intriguing oxidation and reduction chemistry.[16] A particularly active area of study has been that of the photochemically induced charge-separated species for use as catalysis agents and in solar cells.[17]

While studies of these properties in porphyrins have been facilitated by their high solubility in a variety of solvents, similar studies of phthalocyanines have been hindered by their limited solubility in very few solvents. Attempts to solve the solubility problem by attaching sulfate groups on the outer periphery of the

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(1) Schaffer, A. M.; Gouterman, M.; Davidson, E. R. *Theor. Chim. Acta* **1973**, *30*, 9.
(2) McHugh, A. J.; Gouterman, M.; Weiss, C. *Theor. Chim. Acta* **1972**, *24*, 346.
(3) Nyokong, T.; Gasyna, Z.; Stillman, M. J. *Inorg. Chem.* **1987**, *26*, 1087.
(4) Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M. C. *Coord. Chem. Rev.* **1982**, *44*, 83.
(5) Lever, A. B. P.; Licoccia, S.; Ramaswamy, B. S.; Kandil, S. A.; Stynes, D. V. *Inorg. Chim. Acta* **1981**, *51*, 167.
(6) Ohtani, H.; Kobayashi, T.; Ohno, T.; Kato, S.; Tanno, T.; Yamada, A. *J. Phys. Chem.* **1984**, *88*, 4431.
(7) Kobayashi, T.; Nishiyama, T. *J. Phys. Chem.* **1985**, *89*, 1167.
(8) Van Den Brink, F.; Visscher, W.; Barendrecht, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *175*, 279.
(9) Ferraudi, G.; Prasad, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2137.
(10) Prasad, D. R.; Ferraudi, G. *Inorg. Chem.* **1983**, *22*, 1672.
(11) Prasad, D. R.; Ferraudi, G. *J. Phys. Chem.* **1984**, *88*, 4037.
(12) Ohno, T.; Kato, S. *J. Phys. Chem.* **1984**, *88*, 1670.

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fused benzene rings of the phthalocyanine[18-23] do enhance the solubility, but aggregation becomes serious, and the spectroscopic and electrochemical data are much more difficult to interpret. The group I and II metal substituted phthalocyanines (MPc) exhibit high solubility in a much wider range of spectroscopically transparent and electrochemically useful solvents.[24-26]

Although many optical spectra of MPc complexes have been reported, there have been few attempts to assign the electronic transitions that give rise to these spectra.[3,25,27-30] In particular, with the exception of our previous studies on ZnPc[3] and α-phase thin films,[31] no deconvolution calculations have been reported that identify the individual bands that make up a significant fraction of the absorption envelope between 220 and 1000 nm. With spectral envelopes that extend over such a wide spectral range as are observed for MPc complexes, and where the possibilities for photochemistry involving the MPc excited states are so extensive, analysis of the origin of the major spectral intensity is important. As a minimum, an estimation of the number of bands that can contribute to the envelope is necessary before assignment of either the orbital or state to state origin can be attempted. The situation for both the phthalocyanines and porphyrins is complicated because some of the most interesting chemistry takes place with complexes metalated with transition metals,[9-11,32] where charge-transfer transitions overlap the ring $\pi-\pi^*$ transitions, or with oxidized or reduced complexes, where new bands are observed that can arise from internal, ring-based ($\pi-\pi$) transitions.[32] Although many absorption spectra of oxidized MPc complexes have been reported,[26,27,32,33,34] it is only very recently that detailed attempts have been made at assigning any of the bands that are observed.[3,27] These studies on the π-cation species identified a pressing need for a full assignment of the $\pi-\pi^*$ spectral envelope in neutral MPc species.

In this paper, we describe the spectral and electrochemical properties of a range of highly soluble MgPc complexes. MgPc is chemically,[34] electrochemically,[35] and photochemically[36,37] a very interesting molecule, and the data reported in this study can act as a model for the spectral properties of many other MPc species. Deconvolution calculations are used to obtain the energies, bandwidths, and magnetic moments of the transitions that contribute to the observed spectral envelope between 230 and 800 nm.

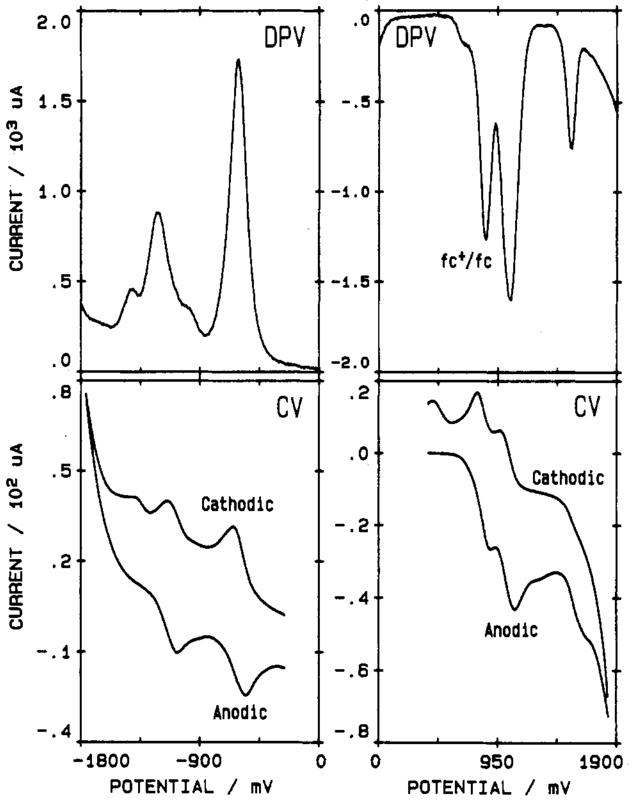

Figure 1. Cyclic voltammograms and differential-pulse voltammagrams of $MgPc(im)_2$ dissolved in DMA containing 0.10 M TPAP. Silver wire was used as an internal reference electrode, while ferrocene was used as an internal standard. The potential axis can be expressed in terms of the saturated calomel electrode (SCE) by using details given in ref 27, 43, and 45. On the basis of the American polarity convention, positive current is cathodic and negative current is anodic.

Experimental Section

Materials and Methods. MgPc was prepared according to literature methods.[38] Imidazole (im; Fisher), sodium cyanide (NaCN; Fisher), pyridine (py; BDH), 4-methylpyridine (mepy; BDH), and methylimidazole (meim; Aldrich) were used without further purification. Tetrapropylammonium perchlorate (TPAP; Kodak) was recrystallized from acetone (BDH). Methylene chloride (BDH) was used without further purification. Dimethylacetamide (DMA; BDH) was distilled before use. The individual $MgPc(L)_2$ (L = im, CN^-, meim, py, mepy) complexes were synthesized as described previously.[25,27] The sharpness of the Q-band-region *A* term (Figure 2) and the similarity between spectra taken in both CH_2Cl_2 and DMA suggest that these complexes are monomeric under the conditions used spectroscopically. The optical spectra were stable, and dissociation of the axial ligands was not observed electrochemically.

Spectroscopic Methods. All spectra were recorded as methylene chloride solutions because the UV operating range is wider for this solvent than for dimethylacetamide (DMA). Absorption spectra were recorded on a Cary Model 219 spectrophotometer. Molar extinction coefficients for the MgPc complexes, MgPc (ϵ_{670} = 217 000 L mol^{-1} cm^{-1}), $MgPc(im)_2$ (ϵ_{670} = 173 000 L mol^{-1} cm^{-1}), $MgPc(meim)_2$ (ϵ_{670} = 150 000 L mol^{-1} cm^{-1}), $MgPc(CN^-)_2$ (ϵ_{670} = 123 000 L mol^{-1} cm^{-1}), $MgPc(py)_2$ (ϵ_{670} = 200 000 L mol^{-1} cm^{-1}), and $MgPc(mepy)_2$ (ϵ_{670} = 245 000 L mol^{-1} cm^{-1}), were determined in dimethylacetamide and were used to assign the concentrations of the $MgPc(L)_2$ samples used in CH_2Cl_2 solutions. Typical concentrations used for spectroscopic measurements were of the order of 8×10^{-6} L mol^{-1} cm^{-1}, which gave maximum absorbances of 1.5

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(13) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982.
(14) Dolphin, D.; James, B. R.; Murray, A. J.; Thornback, J. R. *Can. J. Chem.* **1980**, *58*, 1125.
(15) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. III, Part A, pp 1–165.
(16) Dicken, C. M.; Woon, T. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1636.
(17) McIntosh, A. R.; Siemiarczuk, A.; Bolton, J. R.; Stillman, M. J.; Ho, T.-F.; Weedon, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 7215.
(18) Adzic, R.; Simic-Glavaski, B.; Yeager, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *194*, 155.
(19) Greun, L. C.; Blagrove, R. J. *Aust. J. Chem.* **1973**, *26*, 319.
(20) Lever, A. B. P.; Hempstead, M. R.; Leznoff, C. C.; Liu, W.; Melnik, M.; Nevin, W. A.; Seymour, P. *Pure Appl. Chem.* **1986**, *J58*, 1467.
(21) Nevin, W. A.; Liu, W.; Melnik, M.; Lever, A. B. P. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *213*, 217.
(22) Moxon, N. T.; Fielding, P. E.; Gregson, A. K. *J. Chem. Soc., Chem. Commun.* **1981**, 98.
(23) McLendon, G.; Martell, A. E. *Inorg. Chem.* **1977**, *16*, 1812.
(24) Homborg, H.; Kalz, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1063.
(25) Martin, K. A. M.Sc. Thesis, University of Western Ontario, London, Canada, 1979.
(26) Homborg, H. *Z. Anorg. Allg. Chem.* **1983**, *507*, 35.
(27) Nyokong, T. N. Ph.D. Thesis, University of Western Ontario, London, Canada, 1986.
(28) Edwards, L.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *33*, 292.
(29) Minor, P. C.; Lever, A. B. P.; Gouterman, M. *Inorg. Chem.* **1985**, *24*, 1894.
(30) Lever, A. B. P.; Pickens, S. R.; Minor, P. C.; Licoccia, S.; Ramaswamy, B. S.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800.
(31) Hollebone, B. R.; Stillman, M. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *74*, 2107.
(32) Nyokong, T.; Gasyna, Z.; Stillman, M. J. *ACS Symp. Ser.* **1986**, *No. 321*, 309–327.
(33) Homborg, H.; Kalz, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1067.
(34) Linder, R. E.; Rowlands, J. R.; Hush, N. S. *Mol. Phys.* **1971**, *21*, 417.
(35) Kahl, J. L.; Faulkner, L. R.; Dwarakanath, K.; Tachikawa, H. *J. Am. Chem. Soc.* **1986**, *108*, 5434.
(36) Lever, A. B. P.; Minor, P. C.; Woolsey, I. S. *Inorg. Chem.* **1981**, *20*, 4015.
(37) Gradyushko, A. T.; Sevchenko, A. N.; Solovyov, K. N.; Tsvirko, M. P. *Photochem. Photobiol.* **1970**, *11*, 387.
(38) Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1022.

Table I. Half-Wave Potentials of the MgPc(−2)(L)$_2$ Species Dissolved in DMA Containing 0.10 M TPAP

	$E_{1/2}$/V (fc$^+$/fc)^b	$E_{1/2}$/V (SCE)^b		$E_{1/2}$/V (fc$^+$/fc)^b	$E_{1/2}$/V (SCE)^b
MgPc^a	0.64	1.11	MgPc(py)$_2$	0.69	1.16
	0.18	0.65		0.20	0.67
	−1.37	−0.88		−1.38	−0.91
	−1.86	−1.43		−1.92	−1.45
MgPc(im)$_2$	0.63	1.10	MgPc(mepy)$_2$	0.66	1.13
	0.17	0.64		0.20	0.67
	−1.40	−0.93		−1.29	−0.82
	−1.94	−1.47		−1.76	−1.29
MgPc-(meim)$_2$	0.74	1.21	ferrocene	0.00	0.47
	0.17	0.64			
	−1.39	−0.92			
	−1.86	−1.39			

^{a} Linstead et al.[38] suggest that MgPc will be coordinated by H_2O. ^{b} See ref 45.

in the Q-band region. MCD spectra were recorded at room temperature on a Jasco J500 C spectropolarimeter controlled by an IBM S9001 computer using the computer program CDSCAN5[39] with a field of 5.5 T provided by an Oxford Instruments SM2 superconducting magnet (absorption spectra were recorded from these same solutions). Calibration of the MCD signal intensity was performed by using an aqueous solution of cobalt(II) sulfate with the negative band intensity at 510 nm, as $\Delta\epsilon_M = -1.9 \times 10^{-2}$ L mol^{-1} cm^{-1} T^{-1}.

Data Analysis. Gaussian band shapes were used to fit the absorption and MCD spectra. Fitting was performed by using the program SIMPFIT,[40] which utilizes a Simplex routine to fit the MCD spectra and a least-squares routine to fit the absorption data. The data base management program Spectra Manager[41] was used to manipulate the spectral data, and an HP 7550A digital plotter was used for plotting.

Electrochemistry. The electrochemical measurements were carried out by using a Princeton Applied Research Model 273 electrochemical system controlled by an IBM instruments S9001 computer using the computer program ELECTRA,[42] as previously described.[27,43] Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) experiments on the MgPc complexes were carried out in freshly distilled DMA in the presence of 0.05 M tetrapropylammonium perchlorate (TPAP). All solutions were deoxygenated with dry nitrogen.[44] For CV and DPV experiments, a platinum bead was used as the working electrode, while platinum wire was used as the auxiliary electrode. Silver wire and ferrocene were used as internal standards.[43,45]

Results

I. Electrochemistry. The cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) response curves for MgPc are shown in Figure 1. The results are displayed in Table I together with those for MgPc(L)$_2$ (L = im, meim, py, mepy). MgPc(CN$^-$)$_2$ was not used, since previous studies[43] have suggested that this complex undergoes more complicated chemistry involving the oxidation by organic radicals:

$$[\mathrm{MPc}(-1)] + \mathrm{CN}^- \rightarrow \mathrm{MPc}(-2) + \mathrm{CN}^\bullet$$

$$2\mathrm{CN}^\bullet \rightarrow (\mathrm{CN})_2$$

This reaction depletes the concentration of the Pc π cation radical, and inconclusive results are usually obtained.

The CV and DPV results were obtained DMA, which makes the use of water-based electrodes such as the saturated calomel electrode (SCE) and normal hydrogen electrodes (NHE) impractical. In nonaqueous electrochemistry a liquid-junction potential would occur at the solution interface, causing significant unwanted errors in the recorded potentials. As in previous studies,[43] this problem was overcome by utilizing a silver wire as an internal reference electrode. The ferrocene/ferrocenium (fc$^+$/fc) couple was used to provide internal calibration.[45] The voltages of the CV and DPV results plotted in Figure 1 are referenced to the silver wire electrode.[43] The half-wave potentials recorded in Table I are shown vs the fc$^+$/fc couple and vs the SCE. The values with respect to the SCE were calculated by taking the value for $E_{1/2}$(fc$^+$/fc) as +0.47 V in DMA; these corrected values vs the SCE are used throughout the text.

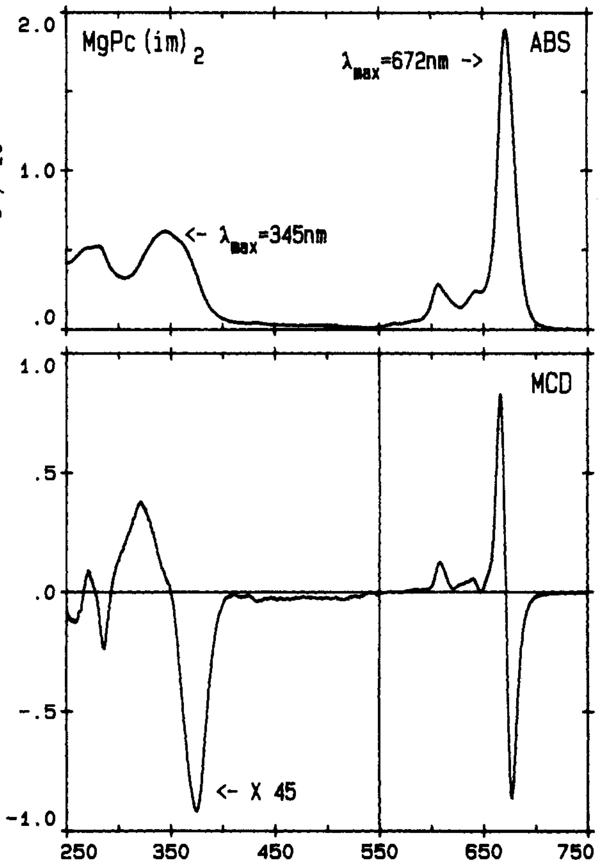

Figure 2. Absorption (ABS) and magnetic circular dichroism (MCD) spectra for MgPc(im)$_2$ in CH_2Cl_2. All spectra were measured in 1 cm path length square UV cells or 1 cm path length cylindrical MCD cells, with maximum absorbances of 1.5 in the Q-band region. The spectra for the other complexes are very similar in the 500–750-nm region. In the 200–500-nm region the envelopes are different for each ligand. The spectral envelopes for each complex can be obtained from Figures 4–7 by extracting the heavy line from the other data.

Figure 1 shows typical, full voltage range CV and DPV curves obtained for the MgPc(L)$_2$ complexes; here data for MgPc in DMA are shown. Both scans can be used to calculate half-wave potentials. The half-wave potentials in Table I were calculated by using the DPV data because superior resolution is obtained in this type of experiment. The peak to trough separations indicate truly reversible electron transfer is taking place.[46] The solutions could be cycled continuously with no loss of peak position, which indicates that no chemical changes were taking place. The data for all the complexes studied exhibited the same overall electrochemical properties with, typically, reduction to [MgPc(−3)]$^-$ at −0.88 V and to [MgPc(−4)]$^{2-}$ at −1.43 V and oxidation to the π-cation-radical species [MgPc(−1)]$^{\bullet+}$ at 0.65 V and to the dication at 1.11 V, all values corrected to be referenced against the SCE (where the nomenclature used to indicate electron distribution between the metal and the π ring follows previous style[43,47]). Clearly, the lack of metal oxidation results in very clean elec-

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(39) Kitchenham, R.; Stillman, M. J., unpublished results.

(40) Browett, W. R.; Stillman, M. J. *Comput. Chem.* **1987**, *11*, 241.

(41) Browett, W. R.; Stillman, M. J. *Comput. Chem.* **1987**, *11*, 73.

(42) Nyokong, T.; Stillman, M. J. *J. Autom. Chem.* **1986**, *8*, 122.

(43) Nyokong, T.; Gasyna, Z.; Stillman, M. J. *Inorg. Chem.* **1987**, *26*, 548.

(44) Minor, P. Ph.D. Thesis, York University, North York, Canada, 1983.

(45) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(46) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980.

(47) Lever, A. B. P.; Licoccia, S.; Magnell, K.; Minor, P. C.; Ramaswamy, B. C. In *Electrochemical and Spectrochemical Studies of Biological Redox Components*; Advances in Chemistry 201; American Chemical Society: Washington, DC, 1982; p 237.

Table II. Observed Maxima in the Absorption Spectra of the $MgPc(L)_2$ Species

$MgPc(L)_2$	λ/nm				
MgPc	670	642	606	345	282
$MgPc(im)_2$	672	643	607	345	281
$MgPc(meim)_2$	672	643	607	345	282
$MgPc(py)_2$	671	642	605	345	282
$MgPc(mepy)_2$	671	642	607	345	282
$MgPc(CN^-)_2$	671	642	606	345	282

trochemical behavior. We can compare these reductions and oxidation potentials with ZnPc(im), where $E_{1/2} = -1.43, -0.98$, and 0.71 V vs the SCE, and with MgTPP,[48] where $E_{1/2} = -1.80$, -1.35, and 0.54 V vs the SCE. The more positive oxidation potential from the MPc species (0.65 V for MgPc and 0.71 V for ZnPc) requires the use in photooxidation reactions[32,43] of electron acceptors that have greater oxidizing power than is needed for the comparable porphyrin complex. Thus CBr_4 has to be used with MgPc and ZnPc, while CCl_4 can be used quite successfully with the porphyrins.[32]

II. Spectral Data. Figure 2 shows the absorption and magnetic circular dichroism (MCD) spectra of $MgPc(im)_2$ in CH_2Cl_2. Absorption band maxima for all the MgPc complexes are listed in Table II. The spectral data for all of the $MgPc(L)_2$ complexes resembled those of the simplest phthalocyanines (no charge transfer between metal and ligand),[25,27,28,49] with a well-resolved Q band, a window at 500 nm, and a series of overlapping bands extending to below 250 nm. Aggregation would be indicated by broadening in the Q-band region; clearly, Figure 2 shows that the Q-band *A* term is very well resolved with no additional low-energy bands present. As before,[3] we are particularly interested in the number of transitions in the region between 220 and 400 nm, as it appears with ZnPc that several degenerate transitions lie in this region.[3] MCD spectra provide transition polarization data directly from the spectra because the ground state is nondegenerate, so only Faraday *A* or *B* terms will be observed.[50] These MCD data resemble closely those reported previously for Li_2Pc[25,49,51] and ZnPc[27,43,52]. The high solubility of MgPc (relative to other MPc's), in a solvent as transparent in the UV as CH_2Cl_2, means that the bands below 300 nm are very well defined in all of these data, allowing the deconvolution analysis to be carried out down to 230 nm. This is considerably lower than we have been able to measure MCD spectra previously and provides a significant improvement in the spectral quality above 240 nm. As is evident from Table II, there is little change in absorption band maxima for the different complexes.

III. Spectral Envelope Deconvolution Calculations. The deconvolution calculations, the "fitting" calculations, were carried out on pairs of associated absorption and MCD spectra, which were separated into the 225–500 and 500–700-nm regions.[3,40,55]

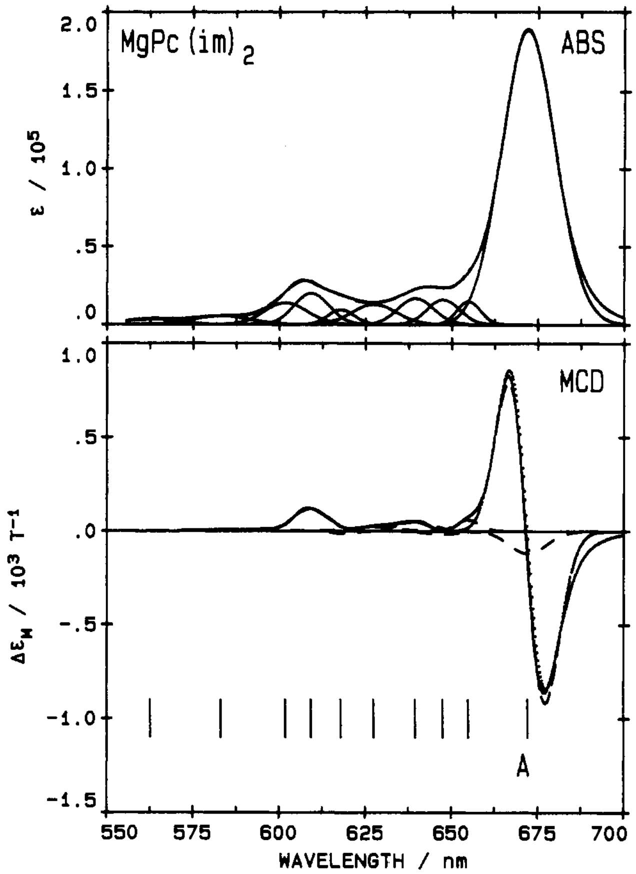

Figure 3. Results of a band analysis for $MgPc(im)_2$ in methylene chloride for the visible region (bands 1–10). Absorption spectra: (—) experimental data; (- - -) fitted data; (—) individual bands. MCD spectra: (—) experimental data; (- - -) fitted data; (···) *A* terms; (– –) *B* terms. The vertical lines that show the band centers of *A* terms are labeled "A".

The visible-region absorption bands are quite isolated from the other degenerate bands and therefore represent a straightforward fitting problem. However, in order to assess the reliability of the Gaussian bands chosen for the fitting, we include Figure 3, which shows the result of a single calculation for the Q band of $MgPc(im)_2$. The fits to the absorption and MCD spectra use the same number of bands, at the same band center and with the same bandwidth, in order to provide severe restrictions on the calculation. In this fit the absorption spectral envelope is filled with 10 Gaussian bands. The 672 nm (14 878 cm^{-1}) band corresponds to both an *A* and a *B* term in the MCD spectrum. The *A* term indicates that the transition giving rise to the band is degenerate.[54] This band is assigned as the Q band.[2,15] The additional *B* term is due to field-induced mixing of the states.[54] Deconvolution yields a series of weak *B* terms in the MCD spectra for the vibrational bands that lie to higher energies of the Q band. Although many different band shapes and combinations of band shapes could be used in these calculations, we feel that the Gaussian shape used here satisfactorily fills the observed envelope without introducing additional variable parameters that the program may end up using to compensate for incorrect numbers of bands. Clearly, this approach is a compromise; however, visual inspection of the band maxima in each of the recorded absorption spectra reveals that the deconvolution calculations place a band where one would expect.

The absorption and MCD spectra in the B-band region (225–400 nm) of the $MgPc(L)_2$ complexes (Figures 4–7) are very complicated. For $MgPc(im)_2$ (Figure 4), we observe several overlapping bands of relatively equal intensity in the absorption spectrum. Deconvolution calculations require 10 bands to fill the spectral envelope. In this region it is the MCD spectrum that provides the necessary and critical information that allows sensible fits to be obtained. Two degenerate transitions, indicated by *A* terms, overlap between 300 and 400 nm. This overlap is a feature

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(48) Felton, R. H. In *The Porphyrins*, Dolphin, D., Ed.; Academic: New York, 1978; Vol. V, pp 53–115.

(49) Martin, K. A.; Stillman, M. J. *Can. J. Chem.* **1978**, *57*, 1111.

(50) The spectra of MCD arise from three different band types[54] known as Faraday *A*, *B*, and *C* terms. *A* terms arise from degeneracy in the excited state, while *C* terms arise from degeneracy in the ground state. *B* terms arise from field-induced mixing of states. The population of degenerate ground states is subject to Boltzmann distribution, which makes the *C* term temperature dependent. The *A* and *B* terms are temperature independent. In an MCD spectrum the *B* terms sum to zero. If the complex has a nondegenerate ground state, then *C* terms will be absent in the MCD spectra. *A* terms are derivative in shape, which distinguishes them from *B* terms.

(51) Stillman, M. J.; Thomson, A. J. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 805.

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

(53) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1984**, *23*, 382.

(54) Piepho, S. B.; Schatz, P. N. *Group Theory in Spectroscopy, with Applications to Magnetic Circular Dichroism*; Wiley: New York, 1982.

(55) The method of moments requires that the transition is isolated so that zeroth and first moments are calculated. Deconvolution uses bands of a fixed shape to fill the spectral envelope. This method requires careful determination of the transition type responsible for the observed intensity but is the only way to fit highly convoluted spectra.

Table III. Band-Fitting Parameters[a] for $MgPc(im)_2$ in CH_2Cl_2

band no.	ν/cm^{-1}	λ/nm	$\Delta\nu/cm^{-1}$	D_0[b]	band type	$\langle\Delta\epsilon_M\rangle_n$[c]	A_1, 10^3B_0[d]	$10^3(B_0/D_0)$	A_1/D_0	μ[e]
1	14874	672	280	16.8	*A*	3340	21 900		1.30	1.21
					B	−2.42	−15.8	−0.94		
2	15270	655	188	0.60	*B*	0.81	5.29	8.81		
3	15445	647	265	0.89	*B*	−0.32	2.08	−2.34		
4	15637	640	295	1.04	*B*	1.05	6.85	6.59		
5	15939	627	385	1.02	*B*	0.61	4.02	3.94		
6	16185	618	232	0.44	*B*	−0.20	−1.29	−2.93		
7	16414	609	321	1.27	*B*	2.50	16.4	12.9		
8	16617	602	402	1.10	*B*	0.06	0.40	0.36		
9	17150	583	536	0.57	*B*	0.29	1.89	3.32		
10	17750	563	511	0.34	*B*	−0.05	−0.30	−0.88		
11	25785	388	2246	1.02	*B*	0.20	1.28	1.25		
12	27451	364	2322	10.1	*A*	1958	12840		1.27	1.18
					B	−0.93	−6.12	−0.61		
13	29463	339	2770	15.6	*A*	1361	8925		0.57	0.53
					B	−0.27	−1.78	−0.11		
14	31584	317	2424	5.31	*B*	0.20	1.31	0.25		
15	33449	299	2255	4.72	*B*	0.27	1.77	0.38		
16	35440	282	2313	9.48	*A*	352	2308		0.24	0.22
					B	−0.27	−1.77	−0.19		
17	37153	269	1831	5.09	*B*	0.008	0.05	0.01		
18	38465	260	1845	3.71	*B*	−0.009	−0.06	−0.02		
19	40319	248	2957	8.51	*A*	561	3676		0.43	0.40
					B	−0.02	−0.12	−0.01		
20	42953	233	2926	7.03	*B*	0.05	0.30	0.04		

[a] Statistics are as follows. B-band region: λ_{23-500} nm, $\chi^2 = 0.50$, $\sum(\Delta\epsilon)^2 = 53.9$. Q-band region: $\lambda_{500-800}$ nm, $\chi^2 = 31.1$, $\sum(\Delta\epsilon)^2 = 86\,880$. [b] $D_0 = \langle\epsilon\rangle_0/326.6$, where the units of D_0 (dipole strength) are D^2 (D : Debye units); 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 MCD. 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 $B_0 = \langle\epsilon_M\rangle_0/152.5$. [d] The units of A_1 are D^2, and the units of B_0 are D^2 cm; see ref 27, p 537. A_1 data are printed above B_0 data when both *A* and *B* terms are used. [e] μ = magnetic moment in units of Bohr magnetrons, μ_B, calculated as $2((A_1/D_0) \times 0.4669)$.

Table IV. Band Centers for the Degenerate Transitions of $MgPc(L)_2$ Species Obtained by the Deconvolution of the Absorption and MCD Spectra

$MgPc(L)_2$	Q	B	N	L	C
MgPc	670	361	338	281	246
$MgPc(im)_2$	672	364	339	282	248
$MgPc(meim)_2$	672	364	339	282	248
$MgPc(py)_2$	671	636	338	282	247
$MgPc(mepy)_2$	671	363	338	282	248
$MgPc(CN^-)_2$	671	363	338	282	247

common across all the MgPc complexes and is found in the UV-region spectra of several other MPc species.[3,27,32,52] The results of the calculations carried out on the MCD spectra for all four samples (Figures 4–7) indicate that there are four degenerate electronic transitions (four linked *A* and *B* terms) in each MCD spectrum. In $MgPc(im)_2$ (Figure 4) the band centers for these transitions were calculated to be 364 nm (27 451 cm^{-1}), 339 nm (29 463 cm^{-1}), 282 nm (35 440 cm^{-1}), and 248 nm (40 319 cm^{-1}). The fitting parameters are summarized in Table III and in Tables VI–X (supplementary material).

IV. Moment Analysis of the Q-Band Region. Table V lists the results of a moment analysis for the Q band in each complexes.[55] The moment calculations were carried out by using the same program as previously;[54] only well-resolved bands can be analyzed in this manner. For our purposes, these moment calculations provide a value for the magnetic moment of the Q-band excited state.[56] The A_1/D_0 parameter factors out any errors in the estimation of the concentration for each solution because the same solution is used for both absorption and MCD measurements.

Discussion

Like MgOEP[57] and MgTPP,[58] MgPc is remarkably photoactive,[37] with the π-cation-radical species being readily generated following illumination by visible-region light. As with many other phthalocyanines, this photoactivity can be understood in terms of the chemistry of the first excited singlet state.[11,59–61] We have in the past been particularly concerned with the photooxidation

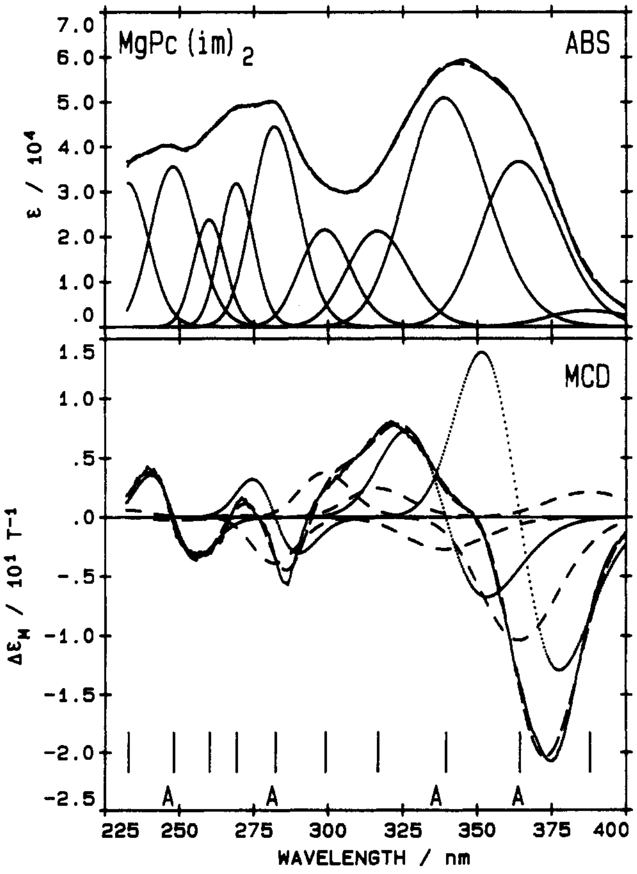

Figure 4. Results of a band analysis for $MgPc(im)_2$ in methylene chloride for the ultraviolet region (bands 11–20). Absorption spectra: (—) experimental data; (- - -) fitted data; (—) individual bands. MCD spectra: (—) experimental data; (- - -) fitted data; (···) *A* terms; (– –) *B* terms. The vertical lines that show the band centers of *A* terms are labeled "A".

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(56) Stephens, P. J.; Suetaka, W.; Schatz, P. N. *J. Chem. Phys.* **1966**, *44*, 4592.

(57) Smalley, J. F.; Feldberg, S. W. *J. Phys. Chem.* **1983**, *87*, 1230.

(58) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1985**, *24*, 2440.

Table V. Moment Analysis of the Q-Band Absorption and MCD Spectra of the $MgPc(L)_2$ Complexes

L[a]	ν/cm^{-1}	D_0[b]	$(\Delta\epsilon_M)_1$	A_1[c]	A_1/D_0	A_1/D_0 ZnPc[3]	magnetic moment[d]	$(\Delta\epsilon_M)_0$	$10^4(B_0/D_0)$
H_2O	15232	18.8	7990	524	2.78		2.60	1.93	6.72
im	15173	23.8	9240	606	2.54	1.51	2.37	0.86	2.37
meim	15172	20.1	7610	499	2.49		2.33	0.98	3.20
CN^-	15205	18.6	7480	491	2.64	3.55	2.47	1.33	4.69
py	15194	32.6	13200	862	2.65	2.62	2.48	3.35	6.75
mepy	15244	65.1	25800	1690	2.60		2.43	1.35	1.36

[a] In methylene chloride. [b] The units of the dipole strength, D_0, are D^2 (D = Debye units); see ref 48. [c] A_1 has the units of D^2, and B_0 has the units of D^2/cm^{-2}. [d] Magnetic moment in units of μ_B, calculated from $2(A_1/D_0 \times 0.4669)$.

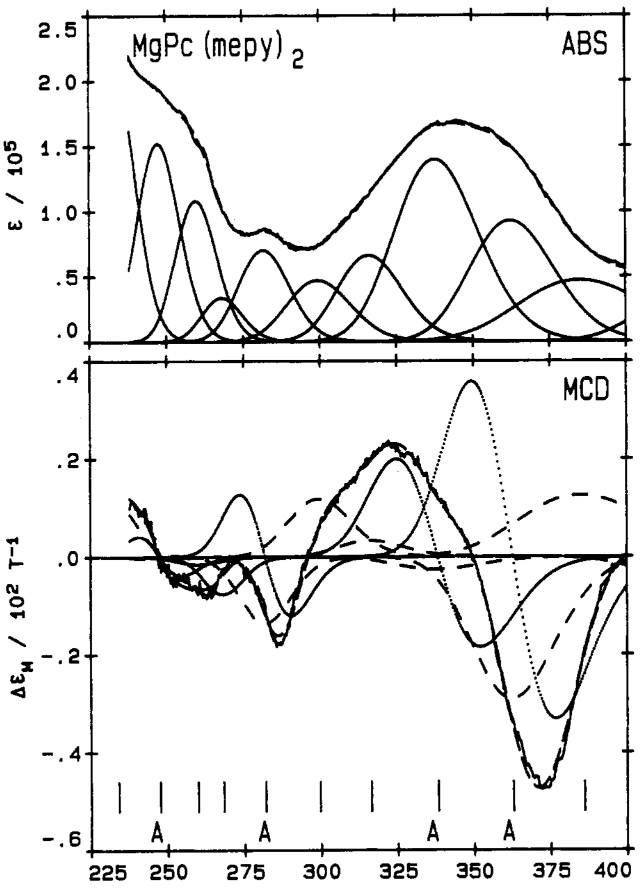

Figure 5. Results of a band analysis for $MgPc(mepy)_2$ in methylene chloride for the ultraviolet region (bands 11–20). Absorption spectra: (—) experimental data; (- - -) fitted data; (—) individual bands. MCD spectra: (—) experimental data; (- - -) fitted data; (···) *A* terms; (– –) *B* terms. The vertical lines that show the band centers of *A* terms are labeled "A".

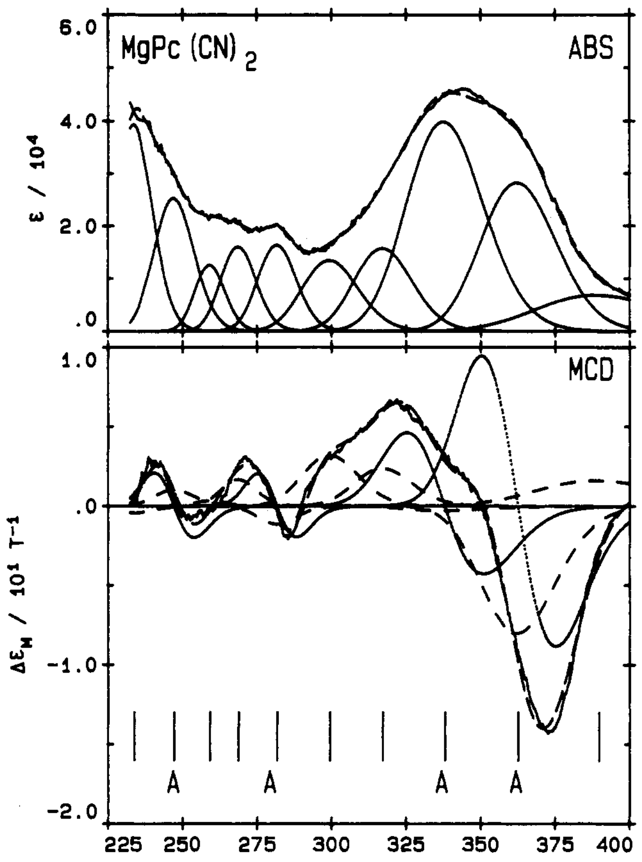

Figure 6. Results of a band analysis for $MgPc(CN^-)_2$ in methylene chloride for the ultraviolet region (bands 11–20). Absorption spectra: (—) experimental data; (- - -) fitted data; (—) individual bands. MCD spectra: (—) experimental data; (- - -) fitted data; (···) *A* terms; (– –) *B* terms. The vertical lines that show the band centers of *A* terms are labeled "A".

properties of MPc complexes in which the π-cation-radical species MPc(−1) is formed.[27,32,43,61] MgPc is particularly attractive because the redox chemistry, as illustrated by the $E_{1/2}$ values, is determined entirely by the ring π electrons, and the π-cation- and π-anion-radical species can be formed readily. However, despite the interest in the photochemical properties of MPc complexes, a general assignment of the absorption bands observed for many MPc species is not available. The problem in the analysis of the spectra of MPc complexes rests with the extensive overlap of transitions associated with the π ring in the 200–450-nm region of the neutral species.[3,27] The absorption spectrum becomes significantly more difficult to assign when extra bands due to charge transfer between the central metal and the ring are also present or when oxidation or reduction of the ring adds new transitions that arise from the partially filled π orbitals.[3,27,32,61]

Recently, we have extended the pioneering studies on the analysis of MPc spectra by Gouterman's group[28] by analyzing the absorption and MCD spectra of neutral and ring-oxidized ZnPc(im).[3] The results obtained in this first full deconvolution calculation carried out over the entire visible–UV range of a monomeric phthalocyanine provided evidence that the absorption maximum near 350 nm comprised two bands, both arising from degenerate transitions. However, because zinc is so large, it sits out of the plane in ZnPc and forms five-coordinate complexes with axial ligands.[62] While CdPc could also serve as a model for simple MPc complexes, we have found that CdPc is not photoactive at all, and we are unable to reproduce the photooxidation properties reported for ZnPc[43] with CdPc. As a result, we have carried out this substantial examination of the absorption and MCD spectra of complexes of MgPc in order to establish the generality of the results reported for ZnPc(im).

Although phthalocyanines exhibit a readily recognizable set of bands that are intense and fairly well resolved between 240 and

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(59) Prasad, D. R.; Ferraudi, G. J. *Inorg. Chem.* **1982**, *21*, 4241.
(60) Prasad, D. R.; Ferraudi, G. J. *J. Phys. Chem.* **1983**, *87*, 4878.
(61) Nyokong, T.; Gasyna, Z.; Stillman, M. J. *Inorg. Chim. Acta* **1986**, *112*, 11.
(62) Barth, G.; Linder, E. B.; Djerassi, C. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1706.

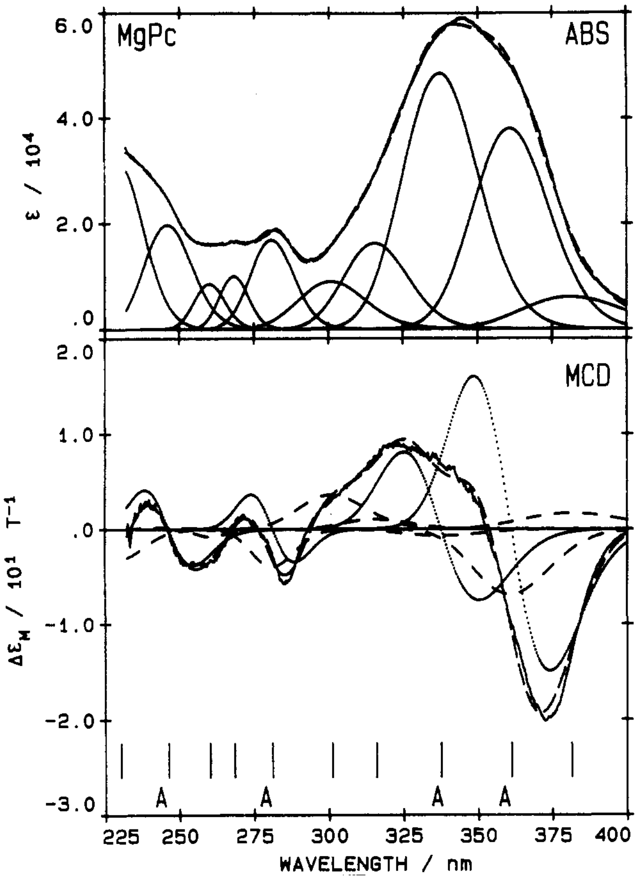

Figure 7. Results of a band analysis for MgPc in methylene chloride for the ultraviolet region (bands 11–20). Absorption spectra: (—) experimental data; (- - -) fitted data; (—) individual bands. MCD spectra: (—) experimental data; (- - -) fitted data; (···) *A* terms; (– –) *B* terms. The vertical lines that show the band centers of *A* terms are labeled "A".

800 nm, it turns out that the assignment of the major spectral features has not been easy. Overlap of all the bands below 400 nm, the appearance of bands related to charge transfer, and the effects of dimerization and aggregation mean that it has been particularly difficult to identify individual bands and to provide good values for band center energies. Traditional methods for increasing spectral resolution by measuring data from crystals or thin films at cryogenic temperatures fail because strong intermolecular interactions result in exciton coupling.[31] The spectra of the solid-state species as thin films are extremely broad and very poorly resolved compared with data recorded from solutions.[31,63–65] Vapor-phase measurements are technically difficult and have not yielded more resolution.[28] In order to obtain high-quality spectral data, the phthalocyanine must be dissolved in solvents transparent between 220 and 400 nm. Unusually for a phthalocyanine, MgPc readily dissolves in solvents like CH_2Cl_2, CH_3CN, 2-propanol, and acetone. We note that the MCD spectra recorded from MPc species deposited in Ar matrices are most likely to provide the best resolution for axially *un*coordinated species,[66] although the chemical probes available to the solution chemist will be lost.[50,51]

Deconvolution of the rich MCD spectra might be expected to yield the required information about each band in the envelope. Unfortunately, deconvolution of spectra that have both positive and negative intensities, like CD and MCD spectra, is very difficult and the results obtained are often ambiguous. We have taken the approach that fitting the absorption and MCD spectra with the same set of bands (with the same centers and widths) is a sufficient additional constraint that results in very much more reasonable fits being obtained. In particular, we have found that the fits obtained in this manner previously for complexes of ZnPc[3] and reported in this work for complexes of MgPc all have bands where one would intuitively place a band. We feel that this is a necessary feature of the fitting procedure.

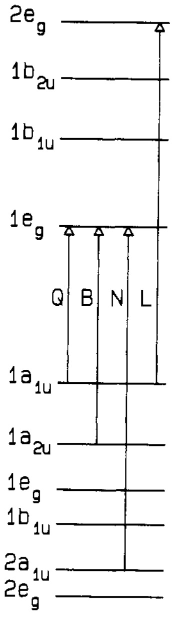

Figure 8. Selected molecular orbitals of the phthalocyanines. The order of the orbitals has been adopted from ref 1, 2, and 15.

I. Comparison between Bands Obtained from the Deconvolution Calculations and Bands Predicted by Theoretical Calculations. The molecular orbitals most usually associated with the bands observed between 250 and 800 nm are shown in Figure 8, in which the transitions were derived from the calculations of Gouterman and co-workers.[2,15] The state picture for both porphyrins and phthalocyanines is considerably more complicated.[15] For the porphyrins, the accidental degeneracy of the two top HOMO's, the a_{1u} and a_{2u} MO's, leads to extensive configuration interaction, resulting in an allowed band, the B or Soret, and a forbidden band, the Q or α/β set.[15] Absorption and MCD spectra of a wide range of substituted metalloporphyrin complexes confirm that the Q-band intensity is highly sensitive to vibronic coupling yet has a high magnetic moment, of about 5 μ_B, associated with it.[15,62] The Q_{00} transition can be readily identified from the MCD spectrum by the presence of its distinctive, positive *A*-term signature, even when the absorption intensity is so low that the band is obscured by the Q_{vib} progression.[53] On the other hand, the Soret band is clearly allowed and is found to have a magnetic moment of about 0.8 μ_B.[15]

For phthalocyanines the situation is quite different. The Q band is clearly the most prominent feature in the spectrum of an "average" MPc complex. MCD spectra show that the magnetic moment is still about 6 times the magnitude of that of the B band (Table V). Significant vibronic effects on the Q band appear to be restricted to the vibrational envelope observed to the blue side of Q_{00}. Unlike the case for the porphyrins, the B band is difficult to find. In the 350-nm region, several broad bands overlap. Depending on the metal, solvent, or axial ligand, one or another of these bands may be more prominent. In addition, charge-transfer bands may overlay this region as well, further complicating the assignment problem.[32,52] Gouterman and co-workers[28] have reported a wide range of MPc spectra using gas-phase studies in order to overcome the notorious insolubility properties of phthalocyanines. In absorption and MCD studies of a series of MPc complexes in DMSO solutions, Stillman and Thomson[52] reported that the second excited state (the B band) was probably located near 370 nm, rather than the 300 nm that would be normally determined from the absorption maximum. MCD spectra[25,49,51] suggested that, for Li_2Pc and ZnPc in DMSO, two

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(63) Sharp, J. H.; Lardon, M. *J. Phys. Chem.* **1968**, *72*, 3230.
(64) Schechtman, B. H.; Spicer, W. E. *J. Mol. Spectrosc.* **1970**, *33*, 28.
(65) Hollebone, B. R.; Stillman, M. J. *Chem. Phys. Lett.* **1974**, *29*, 284.
(66) (a) Misener, G. C.; Schatz, P. N.; Stillman, M. J., unpublished data. (b) Misener, G. C. Ph.D. Thesis, University of Virginia, 1987.

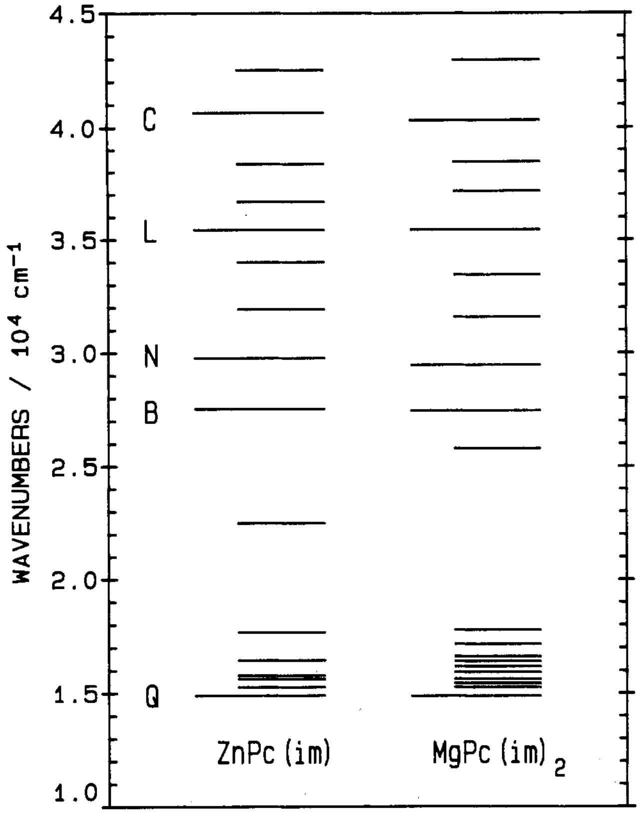

Figure 9. Comparison of the energy levels of MgPc(im)$_2$ and ZnPc(im) calculated by band deconvolution of the absorption and MCD spectra of these two complexes (data for ZnPc(im) replotted from ref 3).

degenerate transitions lay close enough that in many instances the resultant bands would completely overlap. Nyokong et al.[3] confirmed this observation for a series of complexes of ZnPc with spectra recorded in CH_2Cl_2. Full band-envelope deconvolution was shown to be essential in determining the exact band centers from a series of six or seven that overlapped between 240 and 450 nm. The data presented here confirm the earlier observations: the B-band region comprises a series of broad, overlapping bands.

The absorption maxima measured directly from the absorption spectra (Table II) are useful in the identification of phthalocyanines from recorded spectra. However, care should be exercised when these maxima are used to assign band centers. Direct assignment works when the band is either well removed from other bands or significantly greater in intensity than any overlapping bands.

Deconvolution of the B region of MgPc(L)$_2$ (Figures 4–7) emphasizes inadequacies in assigning these spectra directly from band maxima. The results clearly indicate that there are two overlapping bands in this region (with centers near 338 and 362 nm). Deconvolution of the MCD spectra indicated that the two overlapping bands are *A* terms, which are assigned as the B and N bands of the theoretical model.[2,15] The deconvolution yielded two additional *A* terms, which are assigned as the higher energy L and C bands.[3]

II. Comparison between the Deconvolution Data for MgPc and ZnPc. Reproduction of data for one series of complexes by fitting bands to a series of related spectra greatly enhances the reliability of the calculation. An energy level diagram comparing ZnPc(im) and MgPc(im)$_2$ compounds is shown in Figure 9. Focusing on the degenerate transitions, one can see that the results are comparable for zinc and magnesium. In this study we also examined MgPc species with a range of axial ligands. An energy level diagram for the six MgPc species studied is shown in Figure 10. Aside from an additional band (a nondegenerate transition) required for MgPc(mepy)$_2$, all six species required the same number of bands to fit the spectral envelopes. The energies of the bands vary little as a function of the ligand attached to magnesium. The deconvolution results for the six MgPc(L)$_2$ complexes studied are illustrated in terms of an energy level diagram, Figure 10. The similarities in band energies and transition polarizations across these different sets of data are quite apparent. Table IV lists the band centers (in nm) for the degenerate transitions obtained from the deconvolution calculations, rather than directly from the band maxima in the absorption spectra, and assignments based on Gouterman's work (Q, B, N, L, and C bands) are associated with each of these bands.

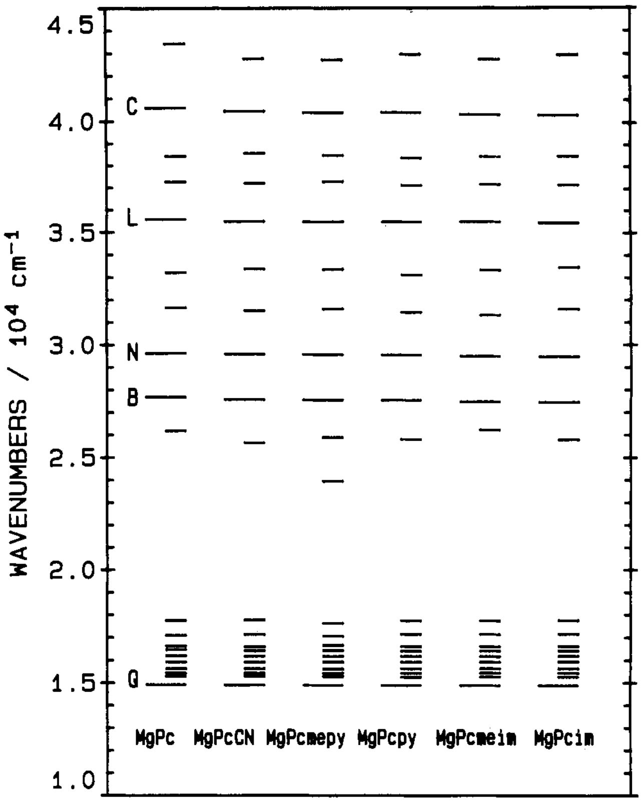

Figure 10. Comparison of the energy levels for MgPc(L)$_2$ calculated from the absorption and MCD data. The wider bars indicate degenerate states. The letters Q, B, N, L, and C are taken from ref 1, 2, and 15.

In Figure 11, the energy difference [ν_{max}(MgPcL$_2$) − ν_{max}(MgPc)] for each of the degenerate bands (Q, B, N, L, and C) is plotted for the six different MgPc(L)$_2$ species. The plot shows that the energies of the degenerate bands decreases across the series: MgPc > MgPc(CN$^-$)$_2$ > MgPc(mepy)$_2$ > MgPc(py)$_2$ > MgPc(meim)$_2$ > MgPc(im)$_2$. The series shows that all the ligated species have band maxima that are red-shifted to varying extents from the MgPc species dissolved in methylene chloride. The Q-band energy is affected the least by the change in the ligand attached to MgPc. The shifts in the band center energy for the B and N bands and the L and C bands are approximately equal for each pair of bands.

Because magnesium is a hard metal, the ligands attached to it should not exert a large effect. Figure 10 shows that this is the case, as there is little difference in the band centers for the six MgPc complexes. The data in Figure 11 show that the band center energies decrease (i.e. red shift) in a sequence that follows a decrease in the σ-donor and π-acceptor strengths in the ligand:[25,43] H_2O > CN$^-$ > mepy > py > meim > im. The insertion of water into the series for the species dissolved in CH_2Cl_2 is necessary because MgPc is strongly hygroscopic. The data in Figure 11 also show that the B and N lines roughly follow the same slope. The effect is also apparent, but not so obvious, for the L and C bands. We believe that the effects seen for the data for these two sets of bands arise from either a coupling between the pairs of energy levels or the use of a common molecular orbital in the construction of the excited states.[15]

Deconvolution calculations carried out for complexes of MgPc, and ZnPc,[3] now readily verify the presence of five degenerate electronic transitions that correspond to the Q, B, N, L, and C bands (or to a set that includes a second B band: Q, B_1, B_2, N,

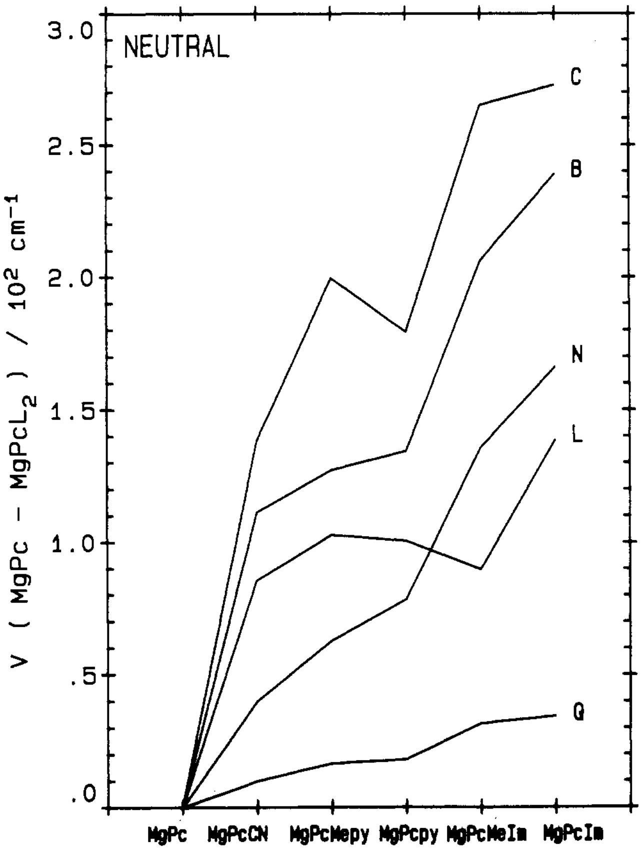

Figure 11. Plot of differences in band centers for each of the five degenerate transitions (Q, B, N, L, C) of the MgPc(L)$_2$ complexes. The energies for the five degenerate bands are subtracted from the reference MgPc compound. This standardizes the $\Delta\nu$ (cm^{-1}) of the five degenerate bands in MgPc at zero.

L, and C[31]). The difficulty arises when one attempts to correlate the energies of these bands with those of the theoretical calculations. Few detailed calculations have been published for the phthalocyanines.[2,15,67] Of these, Gouterman's calculations of the energy levels,[15] and later of the magnetic properties,[2,67] are most useful. The Q band correlates well with these studies, but the B, N, L, and C bands do not match up closely. The major difficulty is the location of the second degenerate transition, at 332 nm.[28] The splitting between the two bands between 330 and 370 nm depends on the axial ligand. The first explanation seems to be that the band center energies for the B, N, L, and C bands had been overestimated by the theoretical calculations. A second possibility was that the degenerate band assigned as B in ZnPc arose from an interaction involving the d electrons of the zinc atom. The energy levels for MgPc(im)$_2$ are compared to those for ZnPc(im) in Figure 10. The plot shows that, aside from the slight effect due to different central metals, the B, N, L, and C band energies are quite similar for the two phthalocyanines. This observation rules out any effect due to the filled d shell of zinc. Curiously, these deconvolution data suggest that the energies of the B, N, and L bands lie remarkably close to those of the same bands predicted for the porphyrins.[68]

In addition to providing more detail in the spectrum, the MCD technique can also be used to provide angular momentum data for excited states as long as the transition is part of an isolated band system.[3,27,52] For phthalocyanines, the Q band is usually completely separate from other bands, including charge-transfer bands. This property means that it is possible to compare the magnetic moments of the excited singlet of a wide range of different MPc complexes. Only Stillman and Thomson[52] and Nyokong et al.[3] have previously published μ_B data for a range of phthalocyanines. The MCD technique does make the determination of these values reasonably straightforward, and with a sufficient range available, interpretation of ring-π-metal orbital interaction should be more reliable than basing such discussion on either band centers or on Q-B splitting energies.

A_1/D_0 values (following the conventions of Schatz[69] and Stephens[70,71]) calculated from the first and zeroth moments of the absorption and MCD spectra, which were obtained by integrating over the whole band envelope in the 500–740-nm region, fall into the range reported previously for ZnPc.[3] The trend in values depends on the axial ligand, as noted previously for a wider range of metals.[27] For MgPc (Table V) we find that the magnetic moment of the S$_1$ state (which gives rise to the Q band) is remarkably constant at about 2.6 (expressed in terms of A_1/D_0). This compares with a range 1.5–3.55 for complexes of ZnPc.[3,27,52] We interpret this variation as a difference in response by the two metals to axial ligation, with interaction between filled d orbitals and the ligand's σ and π orbitals being possible in the Zn but absent in the Mg complexes.

Conclusions

Spectroscopic and electrochemical data are reported for complexes of MgPc in UV-transparent solvents. Quantitative analysis of the absorption and MCD spectra of various liganded species of MgPc indicates the presence of five degenerate transitions. The transitions are assigned as the Q, B, N, L, and C bands. The agreement of these results with those for ZnPc suggests that the differences in covalent radii and coordination geometry, and the presence of filled d orbitals in the zinc, do not affect the π–π^* spectra.

Two effects were observed when the ligand attached to MgPc was varied. As the ligand field strength decreased across the series of ligands, the centers of the Q, B, N, L, and C bands red-shifted. Band assignment for the different ligand species also indicated that the states giving rise to the B and N bands and those giving rise to the L and C bands are coupled to each other.

The analysis suggests that the band centers for the first five bands in the absorption spectrum of phthalocyanines that exhibit no charge-transfer bands or extensive axial ligand effects lie (nm) as follows: 670, Q; 362, B; 338, N; 282, L; 247, C.

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Supplementary Material Available: Additional tables of band-fitting parameters (Tables VI–X) calculated for each of the MgPc(L)$_2$ complexes (except MgPc(im)$_2$) discussed in this study (16 pages). Ordering information is given on any current masthead page.

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(67) Schaffer, A. M.; Gouterman, M. *Theor. Chim. Acta* **1972**, *25*, 62.
(68) Bajema, L.; Gouterman, M.; Rose, C. B. *J. Mol. Spectrosc.* **1971**, *39*, 421.
(69) Schatz, P. N.; McCafferty, A. J. *Q. Rev., Chem. Soc.* **1969**, *23*, 552.
(70) Stephens, P. J. *Chem. Phys. Lett.* **1968**, *2*, 241.
(71) Stephens, P. J. *J. Chem. Phys.* **1970**, *52*, 3489.