Magnetic Circular Dichroism Studies. Part XXIX.[1] Magnetic Circular Dichroism Spectra of Magnesium and Zinc Octaethylporphyrins and their Five- and Six-co-ordinated Complexes

By **Günter Barth, Robert E. Linder, Edward Bunnenberg,** and **Carl Djerassi,*** Department of Chemistry, Stanford University, Stanford, California 94305
Lloyd Seamans and **Albert Moscowitz,** Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

The m.c.d. spectra of zinc and magnesium octaethylprophyrin and their five- and six-co-ordinate complexes with diethyl ether, ethanol, and pyridine are reported at 285 and 77 K. The excited state magnetic moments calculated for the electronic origin of the Q band varied from 2·9 to 5·9 Bohr magnetons depending on the complexation state and central metal. The main effect of the axial ligand is to cause zero-field splitting of the excited state. The magnitude of the splitting varies with the type of axial ligand and is largest for the monopyridine complex of zinc octaethylporphyrin where the separation of the two absorption components is 100 cm^{-1}. The effect is interpreted as the result of the reduction in symmetry from D_{4h} to C_{2v} introduced by the axial ligand.

MEASUREMENTS of the magneto-optical properties of metalloporphyrins have attracted considerable attention recently since the experimentally determined values for the excited state magnetic moments [2,3] can be compared with the values predicted by various theoretical models of the electronic structure of porphyrins.[4-6] On the one hand, the agreement between experiment and theory constitutes an excellent verification of the basic soundness of the theoretical models. On the other hand, these measurements have led to the discovery of zero-field splitting in porphyrins [7] which indicates that further modifications of the theoretical models may be required. Interest has also been stimulated by the observation that m.c.d. appears to be more sensitive to the oxidation state of iron and the particular axial ligands attached to it in heme proteins than is ordinary absorption spectroscopy.[8-12] Since the biological activity of these molecules is strongly influenced by subtle changes in the co-ordination sphere of the heme group, m.c.d. is a particularly pertinent optical method for use in investigations of these proteins.

However, systematic studies of the m.c.d. spectra of model compounds in different complexation states have not been carried out to date. In the present communication we present the results of such a study.

Zinc and magnesium octaethylporphyrin were chosen as model systems for this study since their various complexation states are well known and their electronic spectra are simple in the sense that the transitions observed in the visible and u.v. region of the spectrum are not complicated by charge transfer bands involving the central metal but involve only the π-electron system of the porphyrin ring. Furthermore, since the previously reported m.c.d. and Zeeman measurements of these compounds [3,13] did not explicitly consider changes in their complexation states, a reinterpretation of the conclusions drawn from these studies is desirable.

EXPERIMENTAL

M.c.d. measurements were carried out using a JASCO spectropolarimeter ORD-UV-5 modified for c.d. measurements and to accept a superconducting magnet (Lockheed Palo Alto Research Laboratories, model OSCM-103) [14] capable of producing fields of 49·5 kG. The frequency calibration of the instrument was carried out with a holmium oxide glass (Corning No. 3—138) to an accuracy of ±0·25 nm. The absorption spectra were obtained on a Cary model 14 M spectrophotometer. A special 1 cm brass cell which fits into the bore of the magnet was constructed for the low temperature m.c.d. measurements. Cooling was achieved by flushing precooled nitrogen around the cell wall. By regulating the rate of gas flow the temperature could be adjusted within the range 77—250 K with an accuracy of ±5 K. The temperature was monitored by a copper–constantan thermocouple directly attached to the cell. Low temperature absorption spectra were measured in a 1 cm brass cell immersed in liquid nitrogen.

Magnesium octaethylporphyrin was synthesized from octaethylporphyrin using the magnesium–viologen reagent according to the procedure of Wei *et al.*[15] The product was recrystallized twice from ethanol–cyclohexane and finally sublimed at 250 °C and 10^{-4} mmHg. Zinc octaethylporphyrin was prepared from octaethylporphyrin and zinc acetate by the method of Adler *et al.*[16] and recrystallized twice from benzene–cyclohexane. Both metalloporphyrins were found to be pure by t.l.c. and the possibility of contamination by traces of free base octaethylporphyrin was excluded by absorption spectral measurements. Inform-

---

[1] Part XXVIII, Y. K. Mo, R. E. Linder, G. Barth, E. Bunnenberg and C. Djerassi, *J. Amer. Chem. Soc.*, 1974, **96**, 3309.

[2] P. J. Stephens, W. Suëtaka, and P. N. Schatz, *J. Chem. Phys.*, 1966, **44**, 4592.

[3] E. A. Dratz, Ph.D. Thesis, University of California, Berkeley, 1966.

[4] W. T. Simpson, *J. Chem. Phys.*, 1949, **17**, 1218.

[5] H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, 1950, **18**, 1174.

[6] A. J. McHugh, M. Gouterman, and C. Weiss, *Theor. Chim. Acta*, 1972, **24**, 346.

[7] J. C. Sutherland, D. Axelrod, and M. P. Klein, *J. Chem. Phys.*, 1971, **54**, 2888.

[8] V. E. Shashoua, *Nature*, 1964, **103**, 972.

[9] V. E. Shashoua, *J. Amer. Chem. Soc.*, 1965, **87**, 4044.

[10] B. P. Atanasov, M. V. Volkenstein, and J. A. Sharonov, *Mol. Biol.*, 1969, **3**, 696.

[11] J. Bolard and A. Garnier, *Biochem. Biophys. Acta*, 1972, **263**, 535.

[12] P. M. Dolinger, M. Kielsczewski, J. R. Trudell, G. Barth, R. E. Linder, E. Bunnenberg, and C. Djerassi, *Proc. Nat. Acad. Sci.*, 1974, **71**, 399.

[13] M. Malley, G. Feher, and D. Mauzerall, *J. Mol. Spectroscopy*, 1968, **26**, 320.

[14] S. R. Hawkins and J. H. Harshman, *Rev. Sci. Instruments*, 1967, **38**, 50.

[15] P. E. Wei, A. H. Corwin, and R. Arellano, *J. Org. Chem.*, 1962, **27**, 3344.

[16] A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2443.

ation as to the presence or absence of axial ligands could not be obtained by mass spectrometry since these are lost in the ion source which was kept at 200 °C. For example, the mass spectra of dipyridinemagnesium octaethylporphyrin obtained by recrystallization from pyridine and the sample obtained by sublimation are identical.

The solvents were obtained from the following sources: diethyl ether and pyridine (Mallinckrodt), ethanol (Commercial Solvent Corporation), spectrograde isopentane and methylcyclohexane (MC/B). All solvents were dried over Linde 3A molecular sieves. In addition, methylcyclohexane and isopentane were stored over sodium wire. The concentrations of the metalloporphyrin solutions were 10^{-5}—10^{-6}M. Because of their sensitivity to light, the solutions were kept in actinic glassware and spectra were taken within a few hours of preparation. In particular, solutions of magnesium octaethylporphyrin in hydrocarbon solvents were found to be extremely sensitive to light and care was taken to ensure that these solutions were not exposed to normal laboratory light. The following solvent mixtures for low temperature measurement were used: EPA (diethyl ether–isopentane–ethanol, 5 : 5 : 2 v/v), EPA–pyr (diethyl ether–isopentane–ethanol–pyridine, 12 : 10 : 6 : 0·5 v/v) and MCH–IP (methylcyclohexane–isopentane, 1 : 4 v/v). In order to investigate the possibility that the rigid glass matrix, owing to internal strain, introduces partial depolarization of the circularly polarized light,* we carried out the following experiment. A D-camphor-10-sulphonic acid solution was placed behind the low-temperature cell containing the solvent mixture and the c.d. spectrum was recorded at room temperature and with the low temperature cell cooled to 77 K. For all three solvents used in this study no decrease of ellipticity was observed.

A volume contraction of 30% was taken into account in normalizing the spectra measured at 77 K.[17] The spectra were converted into digital form using a Calma model 302 graphical digitizer. The digitized data were then transferred to the IBM 360/50 digital computer, normalized by standard equations, and plotted on a Calcomp plotter. Molar magnetic ellipticities are given in units of deg cm^2 dmol^{-1} G^{-1}. The $Q(0,0)$ band was fitted using the variable wing model described in a previous paper.[18] Since the resolution between the $Q(0,0)$ band and its vibronic components was greater in the m.c.d. spectrum than in the absorption spectrum the m.c.d. A term was fitted first. The wing parameter (a), half-band width (Γ), amplitude, and centre frequency were allowed to vary freely. Subsequently, the absorption band was fitted using the same wing parameter. The wing parameter a varied from 0 to 0·3 indicating that the band shape approaches more that of a Gaussian distribution than a Lorentzian.

Representative m.c.d. and absorption spectra are shown in Figures 1—4 and the molecular parameters for the $Q(0,0)$ band are collected in the Table.

RESULTS AND DISCUSSION

Complexation States of Zinc and Magnesium Porphyrins.—The complexation behaviour of zinc and magnesium porphyrins has been investigated in detail primarily by means of the changes observed in their absorption spectra in the presence of ligands. In solution zinc porphyrins form five-co-ordinate complexes with a variety of ligands such as amines, alcohols, and ethers.[19-21] Thermodynamically, complex formation is favoured since the equilibrium constant K is of the order of 10^{3}.[19,20] Consequently, the uncomplexed four-co-ordinate species can only be observed in carefully purified and dried hydrocarbon solvents (Figure 1).

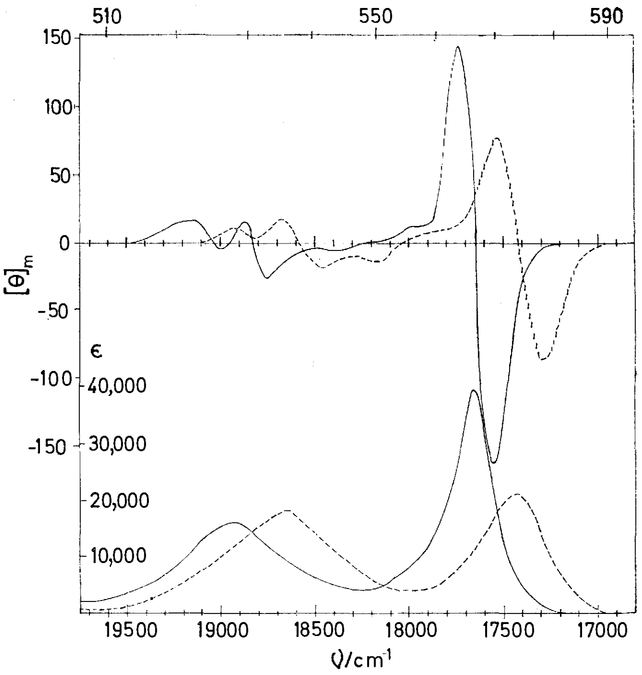

FIGURE 1 M.c.d. and u.v. spectra (lower curves) of zinc octaethylporphyrin in n-octane (——) and ethanol (– – – –) at room temperature

In contrast to the zinc porphyrins where octahedral complexes have not been observed, magnesium porphyrins form both five- and six-co-ordinate complexes.[19,22,23] The equilibrium constant for the attachment of a second axial ligand is, however, 3—4 orders of magnitude smaller than that for the formation of the five-co-ordinate complex for which K is of about the same magnitude as for the zinc porphyrins. This means that even in strongly complexing solvents such as pyridine the equilibrium is shifted only by *ca.* 80% toward the formation of the dipyridine complex. Since the enthalpy of complex formation is negative, lowering the temperature will favour the highest possible complexation state as has been observed for the formation of the copper mesoporphyrin–pyridine complex.[24] The

---

* We are grateful to one of the referees for pointing out this possibility to us.

[17] O. Korver and J. Bosma, *Analyt. Chem.*, 1971, **43**, 1119.

[18] G. Barth, R. E. Linder, E. Bunnenberg, and C. Djerassi, *J.C.S. Perkin II*, 1974, 696.

[19] J. R. Miller and G. D. Dorough, *J. Amer. Chem. Soc.*, 1952, **74**, 3977.

[20] C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, 1969, **8**, 2141.

[21] D. G. Whitten, I. G. Lopp, and P. D. Wildes, *J. Amer. Chem. Soc.*, 1968, **90**, 7196.

[22] C. B. Storm, A. H. Corwin, R. R. Arellano, M. Martz, and R. Weintraub, *J. Amer. Chem. Soc.*, 1966, **88**, 2525.

[23] C. B. Storm and A. H. Corwin, *J. Org. Chem.*, 1964, **29**, 3700.

[24] A. H. Corwin, D. G. Whitten, E. W. Baker, and G. G. Kleinspehn, *J. Amer. Chem. Soc.*, 1963, **85**, 3621.

Molecular parameters for the $Q(0,0)$ band

Compound	Solvent	No. of axial ligands	Temp. (K)	Dipole strength (D^2) [b]	M.c.d. A value (βD^2) [b]	Magnetic moment $\mu(\beta)$ [b]	Centre of frequency of absorption (cm^{-1})	Crossover m.c.d. A term (cm^{-1})	Half-band width Γ (cm^{-1}) m.c.d./u.v.
Magnesium octaethylporphyrin	n-Octane	0	295	3·2	7·6	4·8	17,270	17,285	231/293
	Ethanol	1	295	3·8	7·3	3·8	17,240	17,240	250/357
	EPA	0,1 [c]	295	3·2	6·8	4·3	17,240	17,250	220/284
	EPA	2	77	1·4	2·0	2·9	17,095 17,035	17,065	89/152
	EPA–pyr	1	295	3·9	8·7	4·5	17,250	17,240	271/325
	EPA–pyr	2	77	1·4	2·4	3·4	17,095 17,035	17,050	132/173
	MCH–IP	0	295	3·0	8·8	5·9	17,270	17,270	273/281
	MCH–IP	0	77	2·2	6·2	5·6	17,330	17,330	190/170
Zinc octaethylporphyrin	n-Octane	0	295	6·4	9·7	3·0	17,650	17,635	219/306
	Ethanol	1	295	4·7	9·3	4·0	17,420	17,420	293/412
	Pyridine	1	295	4·1	7·0	3·4	17,315	17,300	287/445
	EPA	1	295	4·0	8·3	4·2	17,420	17,435	282/365
	EPA	1	77	3·4	6·3	3·7	17,495	17,560	140/150
	EPA–pyr	1	295	4·0	7·7	3·9	17,405	17,390	310/439
	EPA–pyr	1	77	3·3	5·0	3·0	17,465 17,360	17,450	174/256
	MCH–IP	0	295	6·2	8·9	2·9	17,665	17,655	220/284

[a] For abbreviations for solvent mixtures see Experimental section. [b] β = Bohr magneton, D = Debye unit. [c] As discussed in ref. 19 the spectral characteristics of the four- and five-co-ordinate magnesium porphyrins are very similar and do not allow a quantitative estimate of the degree of complexation.

solvent systems chosen in this study are such that the complexation state is, in most cases, well defined. The number of axial ligands attached to the central metal are indicated in the Table and require little comment with the exception of magnesium octaethylporphyrin in EPA and EPA-pyr for which the complexation state changes from pyramidal to octahedral on lowering the temperature from 295 to 77 K. The formation of the

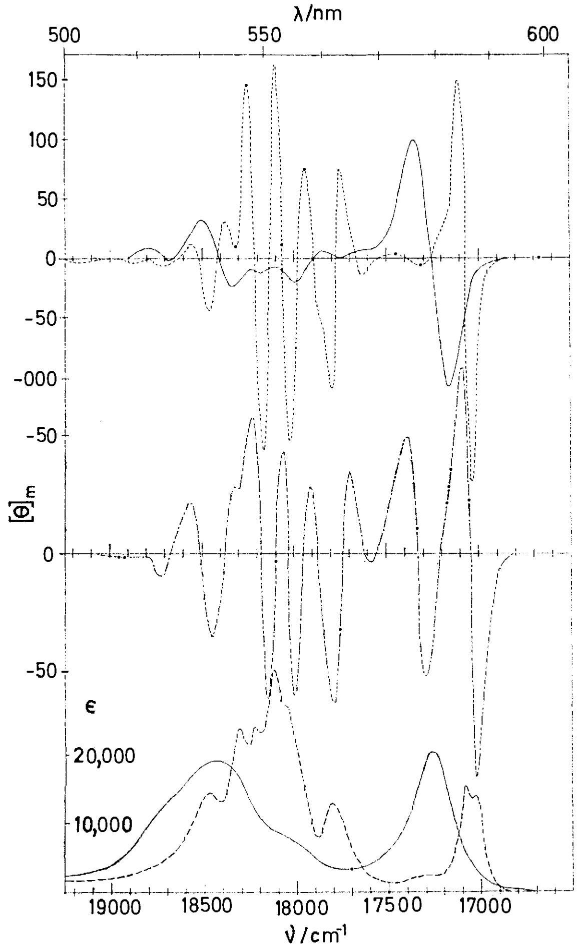

FIGURE 2 M.c.d. and u.v. spectra (lower curves) of magnesium octaethylporphyrin in EPA at room temperature (——) and 77 K (– – – –). Only the m.c.d. spectrum at 140 K (— · — · —) is shown

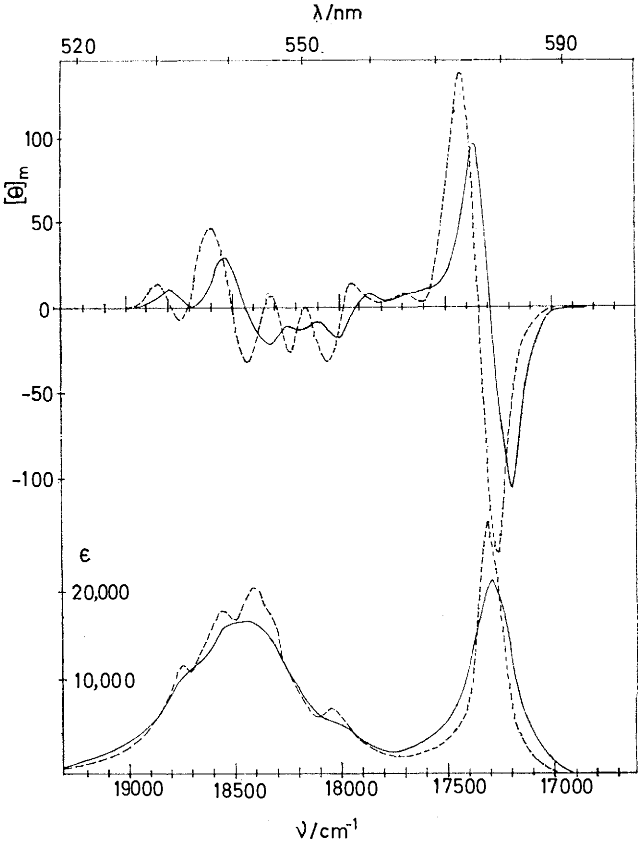

FIGURE 3 M.c.d. and u.v. spectra (lower curves) of magnesium octaethylporphyrin in MCH-IP at room temperature (——) and 77 K (– – – –)

six-co-ordinate species can easily be followed in the m.c.d. spectrum (Figure 2) by the appearance of an *A* term at 17,040 cm^{-1} and the gradual decrease in the intensity of the *A* term at 17,210 cm^{-1} associated with the five-co-ordinate species. Both species are present in roughly equal amounts at 140 K as can be seen in Figure 2 whereas at 77 K the equilibrium is quantitatively shifted to the octahedral complex. These spectral changes are completely reversible when the temperature is allowed to increase. In principle, both ethanol and diethyl ether can participate in complex formation; we believe, however, that the ether complex is favoured because of the higher basicity of the ether oxygen and because of the 2·5-fold excess of ether as compared to ethanol in the solvent mixture. Similar spectral changes were observed in EPA–pyr except that in this case pyridine, because of its much higher basicity, will be the ligand. It was not possible to obtain the low temperature spectrum of the uncomplexed form of zinc octaethylporphyrin in hydrocarbon solvent; whereas the uncomplexed species is clearly the only species present at room temperature (Figure 1), at 77 K, an *A* term at lower frequencies appears which makes an unambiguous interpretation of the low temperature spectrum difficult. Similar experimental results were recently reported for zinc octaethylporphyrin in methylcyclohexane at 140 K and interpreted as being a consequence of dimer formation.[25]

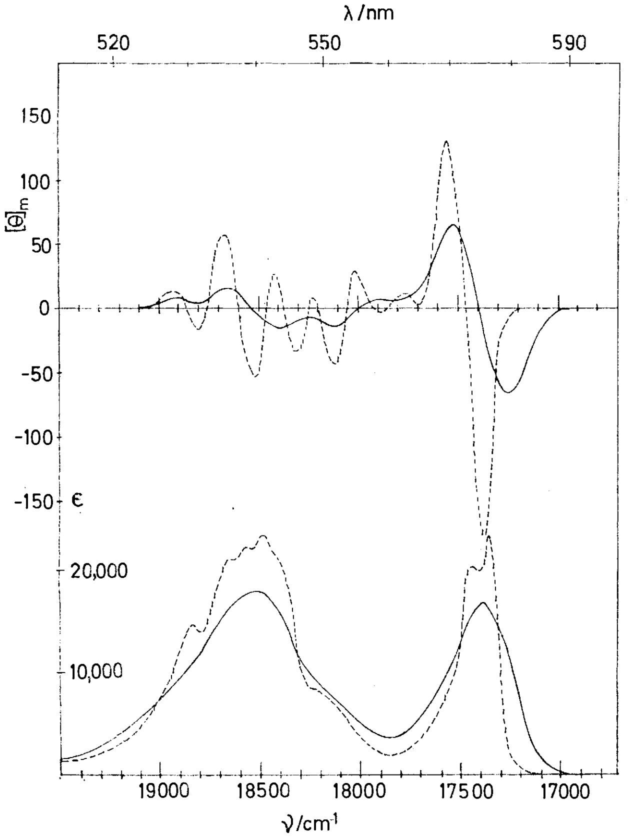

FIGURE 4 M.c.d. and u.v. spectra (lower curves) of zinc octaethylporphyrin in EPA–pyr at room temperature (——) and 77 K (– – – –)

Analysis of Spectra.—The significant parameters that can be extracted from the m.c.d. spectrum of a molecule possessing a doubly degenerate excited state and a non-degenerate ground state are the *A* and *B* values. The m.c.d. *A* value is a function of the excited state magnetic moment whereas the *B* parameter is determined by the amount of interstate mixing caused by the external magnetic field. For an isolated electronic band both parameters are most conveniently obtained through curve fitting procedures as demonstrated by Dratz[3] and Stephens *et al.*[2,26] for the *Q*(0,0) band of metalloporphyrins which is usually well resolved from its vibronic components.[27] The question arises whether this method of obtaining the m.c.d. *A* value is still meaningful in the case where the degeneracy is lifted through a zero-field splitting and the Zeeman splitting becomes a second order effect, *e.g.* is only proportional to the square of the magnetic field strength. As has been shown by Sutherland *et al.*[7] the magnetic moment as determined from the m.c.d. spectrum is fairly insensitive to a splitting that is smaller than the half-band width of the absorption band, a situation which is generally realized in the solution spectra of porphyrins and which therefore justifies the chosen method for determining the magnetic moments.

The *B* values of the compounds investigated in this study were found to be very small and, because of the presence of very intense *A* terms, their absolute values difficult to determine; therefore, only *A* values are given in the Table. The excited state magnetic moments are calculated from the expression $\mu = 2A/D$ (Bohr magnetons).

Ligand-induced Changes in the Q(0,0) *Band.*—We will discuss first the changes that are observed for the *Q*(0,0) band when the fifth and sixth co-ordination sites are occupied by axial ligands. The dipole strengths of the four- and five-co-ordinate complexes of magnesium octaethylporphyrin range from 2·2 to 3·9 D^2 whereas for the octahedral complexes a decrease to 1·4 D^2 was found. For zinc octaethylporphyrin the difference between the uncomplexed and monocomplexed species is more pronounced in that the dipole strength decreases from *ca.* 6·3 to *ca.* 4·0 D^2. Furthermore, the band undergoes a red shift of 200 cm^{-1} as is shown in Figure 1 for the complex with ethanol *versus* the uncomplexed species in n-octane.

The magnetic moments (Table) show considerable scattering and appear to be less sensitive to changes in complexation state. They range from *ca.* 3·8 to 5·4 and *ca.* 3·0 to 4·2 (Bohr magnetons) for the uncomplexed species and the monocomplexes of magnesium and zinc

---

[25] K. A. Zachariasse and D. G. Whitten, *Chem. Phys. Letters*, 1973, **22**, 527.

[26] P. J. Stephens, R. L. Mowery, and P. N. Schatz, *J. Chem. Phys.*, 1971, **55**, 224.

[27] R. E. Linder, G. Barth, E. Bunnenberg, and C. Djerassi, following paper.

octaethylporphyrin, respectively. The octahedral complexes of magnesium octaethylporphyrin were, however, observed to have distinctively lower magnetic moments (2·9 *and* 3·4 Bohr magnetons) compared to the other complexation states of the same metal. Furthermore, in those cases where there was no change in complexation state with temperature, the magnetic moments at 77 K were similar to those at room temperature with the exception of zinc octaethylporphyrin in EPA–pyr where a 20% lower value was found at low temperature. Since in this particular case the zero-field splitting is quite low, it is conceivable that this is due to the inadequacy of the fitting model as pointed out above. In general, therefore, the range of values obtained for the magnetic moment of the first excited state are in very close agreement with the value of 4·3 Bohr magnetons predicted in the SCF–MO–CI calculations of McHugh *et al.*[6]

Malley *et al.*[13] measured the Zeeman splitting of the $Q(0,0)$ band of zinc and magnesium coproporphyrin directly. The calculated magnetic moments were considerably larger than those obtained by m.c.d. for the same compounds. Sutherland *et al.*[7] proposed that this discrepancy between the two techniques could be explained on the basis that the excited state degeneracy is lifted by a zero-field splitting of 50—100 cm^{-1} and pointed out that the Zeeman measurement is more sensitive to slight non-degeneracies than m.c.d. Support for this assumption was recently obtained by van der Waals *et al.*[28,29] who observed a splitting of 109 cm^{-1} in the quasi-line spectrum of zinc porphin in a crystalline n-octane matrix.

We have been able to observe the splitting of the $Q(0,0)$ absorption band directly and our data indicate that the magnitude of the splitting is a function of the complexation state of the metalloporphyrins. In order for the splitting to be observable, the half-band width of the absorption band must be equal to or less than twice the zero-field splitting. The half-band width of the $Q(0,0)$ band in a glass at 77 K was found to be 150—170 cm^{-1} so that a splitting larger than 75—85 cm^{-1} should be detectable. The octahedral complexes of magnesium octaethylporphyrin in EPA and zinc octaethylporphyrin in EPA–pyr are examples where both components are clearly resolved at 77 K (Figures 2 and 4, respectively).

The possibility that the two components of the split $Q(0,0)$ band observed for magnesium octaethylporphyrin (Figure 2) arise from diethyl ether and ethanol complexes, respectively, can be excluded on the grounds that further spectral changes were not observed when the diethyl ether–ethanol ratio was varied from 2·5 to 6 in EPA. Similarly, increasing the concentration of pyridine from 1 to 3 vol % resulted in no spectral alterations of the zinc octaethylporphyrin complex in EPA–pyr at 77 K (Figure 4). Leonard *et al.*[30] recently reported that the formation of dimers of zinc and copper porphins in a hydrocarbon matrix at low temperatures resulted in the splitting of the $Q(0,0)$ band into four components. However dimerization cannot account for the spectral changes observed for magnesium octaethylporphyrin in EPA at 140 K since decreasing the concentration by a factor of 10 did not influence the intensity ratios of the *A* terms at 17,040 and 17,210 cm^{-1} (Figure 2). Vandenbelt *et al.*[31] have shown that when two overlapping bands are just resolved, the observed separation of the two peak maxima is considerably smaller than the actual splitting of the two components. In our case the actual separation is estimated to be *ca.* 40% higher than the observed peak separation. This corresponds to a zero-field splitting of *ca.* 100 cm^{-1} in very good agreement with the value estimated by Sutherland *et al.* from the Zeeman results of Malley *et al.*[13] In contrast, the low temperature spectrum of magnesium octaethylporphyrin in hydrocarbon solvent (Figure 3) shows a single, very sharp $Q(0,0)$ band with a half-band width of 170 cm^{-1} (Table). Since a small unresolved splitting manifests itself as a broadening of the peak maximum, we estimate the zero-field splitting in this case to be considerably less than 85 cm^{-1}. This estimate is in complete agreement with the Shpolskii spectrum of magnesium porphin in n-octane where a splitting of <2 cm^{-1} was observed.[32] Unfortunately, because of the experimental difficulties already noted we could not obtain the low temperature spectrum of the uncomplexed form of zinc octaethylporphyrin and the half-band width (Table) in the room temperature spectrum (Figure 1) is seen that splittings smaller than 140 cm^{-1} cannot be detected.

Therefore only the spectra of monocomplexes of zinc octaethylporphyrins with diethyl ether and pyridine at 77 K are available for comparison. A splitting of 100 cm^{-1} is observed in the absorption spectrum of the pyridine complex (Figure 4), however, the absorption spectrum of the diethyl ether complex exhibits only a single sharp band (Γ 150 cm^{-1}). The only indication for the presence of an unresolved zero-field splitting is the observation that the crossover point of the corresponding m.c.d. *A* term does not coincide with the absorption maximum but is shifted by 65 cm^{-1} to higher frequencies (see Table and Figure 7 of ref. 33). Such a situation is expected to occur when the two components have different absorption intensities as discussed by Sutherland *et al.*[7] In those examples where both components are resolved small differences in intensities are observed, *e.g.* the higher frequency component is of lower intensity in the pyridine zinc octaethylporphyrin complex (Figure 4) but the reverse is observed for the magnesium octa-

---

[28] G. W. Canters, J. van Egmond, T. J. Schaafsma, and J. H. van der Waals, *Mol. Phys.*, 1972, **24**, 1203.

[29] G. W. Canters, J. van Egmond, T. J. Schaafsma, I. Y. Chan, W. G. Van Dorp, and J. H. van der Waals, *Ann. New York Acad. Sci.*, 1973, **206**, 711.

[30] J. J. Leonard and F. R. Longo, *J. Amer. Chem. Soc.*, 1973, **95**, 8506.

[31] J. M. Vandenbelt and C. Henrich, *Appl. Spectroscopy*, 1953, **7**, 173.

[32] A. T. Gadjushko, V. A. Mashenkov, and K. N. Solovyov, *Biofizika*, 1969, **14**, 827.

[33] G. Barth, R. E. Linder, E. Bunnenberg, and C. Djerassi, *Ann. New York Acad. Sci.*, 1973, **206**, 223.

ethylporphyrin dicomplexes (Figure 2). In any case, even if one assumes that the intensity difference is more pronounced in the ether complex of zinc octaethylporphyrin, the zero-field splitting cannot be larger than 80 cm^{-1}. Comparing these results with those of van der Waals *et al.* for zinc porphin [28,29] and assuming that their data are for the uncomplexed species, it appears that the large zero-field splitting of 109 cm^{-1} is caused through the interaction with the crystal lattice and is not representative of the spectral behaviour in solution.

van der Waals *et al.*[28,29] have explained their results as a 'crystal field splitting of the Jahn–Teller unstable ^1E_u state.' In principle a similar interpretation would be given for the observed splitting in the solution spectra. However, since we have found that the magnitude of the splitting is dependent on the presence of a ligand and furthermore varies with the type of ligand, we prefer to interpret the splitting on the basis of symmetry considerations,† which predict that the attachment of a ligand with C_{2v} symmetry will lower the D_{4h} symmetry of the porphyrin thereby causing a splitting of the degenerate excited state. Indeed, Maggiora [34] has recently carried out MO calculations on magnesium porphyrin and its monoaquo complex which for the first time include the effect of an axial ligand with C_{2v} symmetry. It was found that the two highest occupied MOs of e symmetry undergo a small splitting as a result of the lowering of the symmetry introduced by the ligand. Although the calculations did not include the lowest empty MOs it can be assumed that the same effect would have been obtained for the doubly degenerate e_g (π^*) orbital.

In the case of the dicomplexes, it is possible for the symmetry planes of the two ligands to be mutually orthogonal to each other and to the plane of the porphyrin ring, leading to D_{2d} symmetry for the complex. In this point group the e_g (π^*) orbital remains degenerate and we would expect no splitting of the $Q(0,0)$ band. The fact that we observe appreciable zero-field splitting for both octahedral complexes of magnesium octaethylporphyrin thus leads to the conclusion that their symmetry is lower than D_{2d}. Furthermore, the splitting should be directly related to the extent of the interaction of the ligand with the porphyrin π-electron cloud. This would explain the larger splitting observed for pyridine zinc octaethylporphyrin complex compared to the other complex. In connection with this interpretation, it is interesting to note that Estabrook [35] has observed that the splitting of the $Q(0,0)$ band of a number of cytochromes from different sources varies from 75 to 135 cm^{-1}, which, in the light of our results, suggests that either different ligands are supplied by the protein portion or their position with respect to the porphyrin molecule is altered due to the differing steric requirements imposed by the protein chain.

Finally, we would like to comment on an observation we have made previously for a number of porphyrin dications and dianions,[18] namely, that the half-band width is consistently smaller in the m.c.d. spectrum than in the absorption spectrum. An extreme example is magnesium octaethylporphyrin in EPA at 77 K (Figure 2) where $\Gamma_{\mathrm{m.c.d.}}$ is almost one-half of $\Gamma_{\mathrm{u.v.}}$ (Table). This is evidenced by the much higher resolution of the vibronic bands in the m.c.d. spectrum as compared to the absorption spectrum. A rationale for this observation can be given by assuming that the random interaction with the solvent causes a wide range of zero-field splittings and that the fraction of molecules which are strongly perturbed by the solvent contribute proportionally less to the m.c.d. than to the absorption intensity.

Conclusions.—From our results we conclude that the attachment of one or two axial ligands of C_{2v} symmetry will lift the degeneracy of the lowest empty e_g (π^*) MO leading to a zero-field splitting of the first excited state, an effect that has previously been observed for magnesium and zinc porphyrins but has been left unexplained. The strongest evidence for this interpretation is obtained from a comparison of the tetrahedral and octahedral complexes of magnesium octaethylporphyrin at 77 K where only the latter exhibits an observable splitting of the $Q(0,0)$ band. We suggest that the same interpretation can be applied to zinc octaethylporphyrin where the monopyridine complex exhibits a zero-field splitting but the large half-band width of the uncomplexed species at room temperature precludes an estimate whether a splitting is present or not.

We thank the National Institutes of Health and the National Science Foundation for partial support of this work. We thank Professor M. Gouterman for discussions and samples of zinc and palladium porphin. We also thank Professor H. H. Inhoffen for his donation of octaethylporphyrin, and the Stanford Center for Information Processing for their donation of computer time.

[4/518 *Received, 15th March, 1974*]

---

† One of the referees has suggested that it is possible to explain these observations as being due to vibronic Jahn–Teller effects. However, in view of the observed sensitivity to ligands we believe that the static ligand effect outweighs the vibronic effect.

[34] G. M. Maggiora, *J. Amer. Chem. Soc.*, 1973, **95**, 6555.

[35] B. Chance, R. W. Estabrook, and T. Yonetani in 'Hemes and Hemoproteins,' Academic Press, New York, 1966, p. 405.