Spectroscopic characterization of iron complexes of methyl pheophorbide with pyridine and its derivatives

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Abstract

A series of (methyl pheophorbide a)iron(II) and -iron(III) complexes have been prepared and characterized by Mössbauer, ^{1}H NMR and electronic spectra. The central iron(III) ion in (methyl pheophorbide a)iron(III) chloride [Fe(mepheo-a)] is in the high-spin state. Autoreduction of the central iron(III) ion in Fe(mepheo-a)Cl is induced by pyridine (py) and its derivatives (4-Xpy). A connection between isomer shifts and quadrupole splittings of Fe(mepheo-a)(4-Xpy)$_2$ indicates the σ-donation from the axial ligands to the central iron(II) ion is predominant in the axial bonding. The linear dependence of the isomer shifts on Hammett's constants of the pyridine substituents (X) and on the pK_a values of the free ligands reveals that the π-backdonation to the axial ligands enhances synergetically the σ-donation to the central iron(II) ion. The linear correlation between the isomer shift and the electronic absorption wavelength demonstrates that the difference in the π-backdonation to the axial ligands affects the π–π* excitations on the chlorin ring via the central iron(II) ion.

Introduction

The electronic structure of iron porphyrins has been widely investigated by their Mössbauer [1] and electronic [2] spectra. In spite of a great deal of interest in iron porphyrins, there have been few spectroscopic studies on iron chlorins in which the double bond of the four pyrrole rings of the iron porphyrin is saturated [3–7]. In particular, there have been very few Mössbauer studies on iron chlorins. The chlorophyll derivatives such as iron pheophytins [8–10] and iron methyl pheophorbides are typical iron chlorins. These iron chlorins derived from chlorophylls have a fifth isocyclic ring (cyclopentenone ring) in addition to the saturated pyrrole ring. Therefore, it is of interest to clarify the bonding properties of iron chlorins such as iron methyl pheophorbides. In the present work, we discuss the electronic structure of (methyl pheophorbide a)iron(III) chloride [Fe(mepheo-a)Cl], of which the chemical structure is shown in Fig. 1, in comparison with that of the corresponding iron porphyrins and iron pheophytins. It is demonstrated that the central iron(III) ion in Fe(mepheo-a)Cl is autoreduced by pyridine (py) and its derivatives (4-Xpy, where X = CN, COCH$_3$, COOCH$_3$, Cl, CH$_3$). In addition, we describe the bonding

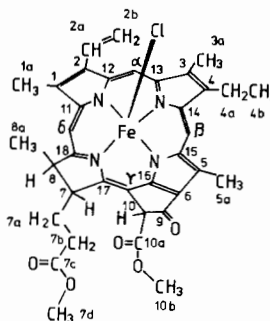Fig. 1. Structure of Fe(mepheo-a)Cl.

between the central iron(II) ion and the axial ligands in these bis-adducts.

Experimental

Materials

Reagents and solvents were of the highest purity commercially available from Wako Pure Chemical Industries, Tokyo Kasei Kogyo Co. Ltd. and Kokusan Chemical Works Ltd. All solvents were deoxygenated prior to use with a stream of dry argon. The water content of chloroform and pyridine was less than 0.003%. Pyridine-d$_5$ (100%) and chloroform-d (99.8%) were

purchased from Aldrich Chemical Company. 4-Chloro-pyridine was prepared by the treatment of 4-chloro-pyridine hydrochloride with sodium carbonate [11].

Preparation of methyl pheophorbide a

Methyl pheophorbide a (H_2mepheo-a) was obtained by the literature method [12] with some modification as follows. Chlorophyll a (100 mg) was dissolved in methanol (10 cm^3). To this solution was added a methanol solution (5 cm^3) of hydrogen chloride (5%) and the solution was refluxed for 1.5 h in an argon atmosphere. After cooling, the solution was diluted with diethyl ether (30 cm^3) and washed with water (20 cm^3 each) three times. Then the ether layer was concentrated and diluted with petroleum ether. The precipitate obtained was collected and dried under vacuum. Finally the product was purified by preparative reversed-phase HPLC with an eluent of acetonitrile/water (95/5, vol./vol.) containing 1% acetic acid. The yield was about 60% after preparative HPLC. ^1H NMR ($CDCl_3$) $\delta = 9.51$ (1H, s, β-meso-H), 9.37 (1H, s, α-meso-H), 8.56 (1H, s, δ-meso-H), 7.98 (1H, X of ABX, 2a-H), 6.32, 6.22 (each 1H, AB of ABX, 2b and 2b'-H), 6.31 (1H, s, 10-H), 4.45 (1H, m, 8-H), 4.20 (1H, m, 7-H), 3.87 (3H, s, 10b-CO_2CH_3), 3.68 (3H, s, 7d-OCH_3), 3.67 (2H, q, $J = 8$ Hz, 4a-CH_2), 3.57 (3H, s, 5a-CH_3), 3.40 (3H, s, 1a-CH_3), 3.22 (3H, s, 3a-CH_3), ~2.62 (2H, m, 7a-CH_2), ~2.28 (2H, m, 7b-CH_2), 1.81 (3H, d, $J = 7$ Hz, 8a-CH_3), 1.69 (3H, t, $J = 8$ Hz, 4b-CH_3), 0.54, −1.62 (each 1H, br, s, N-H).

Preparation of Fe(mepheo-a)Cl

All operations were performed in dim light. The ligand H_2mepheo-a (10 mg, 1.65×10^{-5} mol) was dissolved in acetone (2.5 cm^3). To this solution was added a methanol solution (2.5 cm^3) of $FeCl_2 \cdot 4H_2O$ (33 mg, 1.65×10^{-4} mol). For the Mössbauer measurement, $^{57}FeCl_2 \cdot 4H_2O$ was used. The solution was heated at 60 °C for 3 h in an argon atmosphere, then cooled to room temperature. The iron complex Fe(mepheo-a)Cl was extracted with dichloromethane (10 cm^3) and washed with an aqueous solution (10 cm^3) saturated with NaCl three times. The complex obtained was purified by preparative reversed-phase HPLC with an eluent of acetonitrile/acetone (70/30, vol./vol.) containing tetramethylammonium chloride (1×10^{-3} mol dm^{-3}). In order to remove the tetramethylammonium chloride from the fraction obtained, the dichloromethane solution of the complex was transferred into a separatory funnel and then washed with water. Finally, the complex was recrystallized from dichloromethane/methanol. The yield of Fe(mepheo-a)Cl was about 75% after preparative HPLC and recrystallization. *Anal.* Found: C, 60.31; H, 5.28; N, 7.82. Calc. for $C_{36}H_{36}N_4O_5FeCl \cdot H_2O$: C, 60.55; H, 5.36; N, 7.85%.

Preparation of Fe(mepheo-a)(4-Xpy)₂

Only a representative method is described for Fe(mepheo-a)(py)$_2$ because the preparative methods were similar in all cases. The bis(pyridine) adduct Fe(mepheo-a)(py)$_2$ was prepared by the following two methods, i.e. methods I (autoreduction method) and II (heterogeneous reduction method with sodium dithionite).

Method I. The complex Fe(mepheo-a)Cl (5 mg, 7.0×10^{-6} mol) was dissolved in a mixture of deoxygenated pyridine (0.2 cm^3) and chloroform (2.5 cm^3). The solution was heated at 60 °C for 2.5 h, then cooled to room temperature. For the Mössbauer measurement, the solution was poured into a capsule made of polyethylene resin after the removal of most of the chloroform, and frozen by liquid nitrogen. A dilute solution (about 1×10^{-5} mol dm^{-3}, pyridine/chloroform = 1/5 vol./vol.) was prepared for the measurement of the electronic spectrum. For preparing a ^1H NMR sample, pyridine-d_5 and chloroform-d were used in place of the usual pyridine and chloroform, and a concentrated solution (about 0.01 mol dm^{-3}, pyridine-d_5/chloroform-d = 1/5 vol./vol.) was poured into an NMR tube. All operations were performed in the absence of light and in an argon atmosphere. The reaction product was identified by its ^1H NMR, Mössbauer and electronic spectra.

Method II. The complex Fe(mepheo-a)Cl (5 mg, 7.0×10^{-6} mol) was dissolved in chloroform (2.5 cm^3). To this solution was added pyridine (0.2 cm^3) and an aqueous solution (0.03 cm^3) of sodium dithionite (20 mg). The solution was degassed by freeze–pump–thaw cycles and then stirred for 2.5 h. The product was identified by ^1H NMR, Mössbauer and electronic spectra.

Physical measurements

Electronic spectra were recorded on a Hitachi U-2000 spectrophotometer. ^1H NMR spectra were recorded on a JEOL JNM-GSX 270 FT spectrometer. Mössbauer spectra were measured with a ^{57}Co source (4×10^8 Bq) in a palladium matrix using a Wissel constant-acceleration transducer. The absorber was cooled to 4.2 and 77 K with a Torisha cryostat. The spectra obtained were fitted to Lorentzian curves with a least-squares fitting program. The isomer shifts were referred to the centroid of the Mössbauer spectrum of metallic iron at room temperature. The velocity scale was calibrated by the spectra of metallic iron.

Results and discussion

Electronic structure of Fe(mepheo-a)Cl

The Mössbauer spectra of Fe(mepheo-a)Cl at 4.2 and 298 K are shown in Fig. 2. The Mössbauer pa-
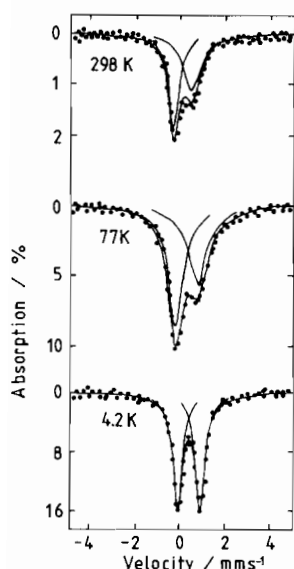
Fig. 2. Mössbauer spectra of Fe(mepheo-a)Cl.

TABLE 1. Mössbauer parameters for Fe(mepheo-a)Cl, high-spin iron(III) pheophytins and high-spin iron(III) porphyrins

Compound	Temperature (K)	δ (mm s^{-1})	ΔE_q (mm s^{-1})
Fe(mepheo-a)Cl[a]	298	0.22(7)	0.80(4)
	77	0.36(9)	0.86(9)
	4.2	0.41(4)	1.00(0)
Fe(pheo-a)Cl[b]	4.2	0.41	1.05
Fe(pheo-b)Cl[b]	4.2	0.42	1.09
Fe(pp)Cl[c]	4.2	0.35–0.41	0.62–1.02
Fe(oep)Cl[c]	4.2	0.41	0.93
Fe(tpp)Cl[c]	4.2	0.41	0.46
Fe(pclpp)Cl[c]	4.2	0.44	0.73

[a]Estimated uncertainties were ±0.008 mm s^{-1}. [b]Taken from ref. 8. Abbreviations: pheo-a, dianion of pheophytin a; phe-b, dianion of pheophytin b. [c]Taken from ref. 1. Abbreviations: pp, dianion of protoporphyrin IX; oep, dianion of octaethylporphyrin; tpp, dianion of tetraphenylporphyrin; pclpp, dianion of 4-chlorophenylporphyrin.

rameters, isomer shifts (δ) and quadrupole splittings (ΔE_q) are summarized in Table 1 together with those of the corresponding iron(III) porphyrins [1] and iron(III) pheophytins [8]. The Mössbauer parameters obtained indicate that the central iron(III) ion in Fe(mepheo-a)Cl is in the high-spin state. As shown in Fig. 2, the spectrum at 4.2 K consists of a well-resolved symmetric pair. In contrast, the spectra at 77 and 298 K were broadened at the positive velocity side. However the two lines of the quadrupole doublet have equal area at each temperature. The phenomenon observed here is similar to that observed for (protoporphyrin IX)iron(III) chloride [1]. This is interpreted as follows [13]. The degeneracy of the sextet of the iron(III) ion is partly removed by the interaction between the electron

spin ($S = 5/2$) and axial ligand field. In such case, the sextet is split into three Kramers doublets, i.e. $S_z = \pm 5/2$ (energy: 6D, D = axial ligand field parameter), $\pm 3/2$ (energy: 2D) and $\pm 1/2$ (energy: OD). The relaxation for the $S_z = \pm 1/2$ ground state is rapid compared to the Mössbauer lifetime, while that for $S_z = \pm 3/2$ and $\pm 5/2$ excited states is slow. At 4.2 K, the spectrum is symmetric because the ions only populate the $S_z = \pm 1/2$ ground state. As the temperature increases, the $\pm 3/2$ and $\pm 5/2$ excited states are thermally populated. Hence the spectra at higher temperature become asymmetric due to magnetic hyperfine interaction. In other words, spin–spin relaxation between the members of $S_z = \pm 1/2$ is fast and hence the spectrum becomes symmetric. The more slowly relaxing $\pm 3/2$, $\pm 5/2$ excited states are populated at higher temperatures, so that the spectrum becomes asymmetric because of a superposition of the spectra originating from ions in the ground and excited states. Comparing the Mössbauer parameters of Fe(mepheo-a)Cl with those of corresponding iron porphyrins, the isomer shifts are similar to those for iron porphyrins. On the other hand, the quadrupole splittings are larger than those for iron porphyrins. This indicates that the presence of a cyclopentenone ring and a saturated pyrrole ring in Fe(mepheo-a)Cl causes more asymmetric arrangement of charges on the ligand. The isomer shift of Fe(mepheo-a)Cl at 4.2 K is almost identical with that of the iron complex of pheophytin a, i.e. Fe(pheo-a)Cl. The replacement of a phytyl group (long carbon chain) by a methyl group hardly influences the s-electron state of the central iron(III) ion. The quadrupole splitting at 4.2 K is slightly smaller than that for Fe(pheo-a)Cl, indicating that the replacement of the substituent enhances the symmetry of the arrangement of charges around the iron(III) ion.

The electronic spectrum of Fe(mepheo-a)Cl is shown in Fig. 3 together with that of Fe(pheo-a)Cl [9]. The strong absorption between 350 and 400 nm is assigned to the Soret band and that near 600 nm is due to the Q band. The spectral features are quite similar to those of Fe(pheo-a)Cl. Thus, the π–π^* excitations on the
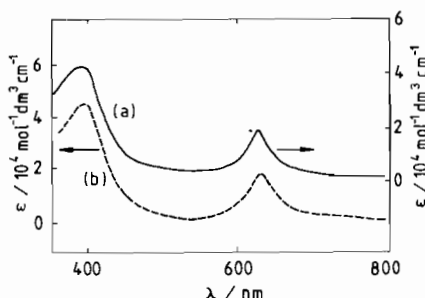

Fig. 3. Electronic spectra of Fe(mepheo-a)Cl (a) and Fe(pheo-a)Cl (b).

chlorin ring are not influenced by the replacement of the substituent.

Preparation of Fe(mepheo-a)(py)₂

The ^{1}H NMR data of the sample prepared by heating with pyridine (method I) are shown in Table 2. Heating with pyridine led to dramatic changes of the chemical shifts. Although the peaks of Fe(mepheo-a)Cl have large paramagnetic shifts, the peaks of the sample prepared by method I do not have any paramagnetic shift and the positions of the peaks agreed with those of the sample prepared by reduction with sodium dithionite (method II). In addition, the spectral features were similar to those of H₂mepheo-a. These facts indicate that the high-spin Fe(III)(mepheo-a)Cl is autoreduced to the low-spin Fe(II)(mepheo-a)(py)₂ by heating with pyridine. Autoreduction in the presence of pyridine has been found in some iron porphyrins [14–21]. However, the autoreduction in most cases of iron porphyrins requires photoirradiation [14–17] or addition of hydroxide [17], and thermal reduction yields a very small amount of iron(II) species [14]. Furthermore, the reduction in pyridine–chloroform is minimal [18]. These results in iron porphyrins are in contrast to the results of the present study. Although the reducing agent in the present case is not identified, the auto-

reduction of Fe(mepheo-a)Cl proceeds by very similar pathways for a variety of ferric porphyrins. The spectrum of Fe(mepheo-a)(py)₂ indicates the presence of two species. This is not surprising because chlorophyll a and its derivatives, e.g. pheophytin a, have two epimers at the C-10 position in the basic solution containing pyridine [22, 23], i.e. (10R)-configuration and (10S)-configuration. Hence the two species obtained here are (10R)-Fe(mepheo-a)(py)₂ and (10S)-Fe(mepheo-a)(py)₂.

The autoreduction is also well-confirmed by the Mössbauer spectra. The spectrum (77 K) of the sample prepared by method I is shown in Fig. 4. The spectrum became a well-resolved symmetric pair by treatment with pyridine. This spectrum is almost identical with that of the sample prepared by method II, indicating that the high-spin Fe(III)(mepheo-a)Cl is autoreduced to the low-spin Fe(II)(mepheo-a)(py)₂. The Mössbauer parameters of Fe(mepheo-a)(py)₂ are listed in Table 3 with those of some low-spin bis(pyridine) adducts of iron(II) porphyrins [1]. The autoreduction is supported by the fact that the parameters of the Fe(mepheo-a)(py)₂ are similar to those of iron(II) porphyrins. The electronic spectra of Fe(mepheo-a)Cl and the sample prepared by method I are shown in Fig. 5. The electronic spectrum of the sample prepared by method I agrees

TABLE 2. ^{1}H NMR data of Fe(mepheo-a)(py)₂ (pyridine-d₅/chloroform-d = 1/5 vol./vol.; J(Hz))

δ^a	Multiplicity^b	Assignment
(10R)-Fe(mepheo-a)(py)₂		
9.13	s	β-meso-H
9.03	s	α-meso-H
8.04	s	δ-meso-H
7.75	X of ABX	2a-H
5.69	AB of ABX	2b-H
5.43	AB of ABX	2b'-H
5.68	s	10-H
4.21	m	8-H, 7-H
3.55	s	10b-CO₂CH₃
3.35	q, $J=6$	4a-CH₂
3.33	s	7d-OCH₃
3.22	s	5a-CH₃
2.90	s	1a-CH₃
2.90	s	3a-CH₃
~2.15	m	7a-CH₂
~1.98	m	7b-CH₂
1.82	d, $J=6$	8a-CH₃
1.35	t, $J=7$	4b-CH₃
(10S)-Fe(mepheo-a)(py)₂^c		
7.92	s	δ-meso-H
5.89	s	10-H
3.44	s	10b-CO₂CH₃

^{a}Shift in ppm from TMS. ^{b}s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{c}Other chemical shifts were identical with those of (10R)-Fe(mepheo-a)(py)₂.
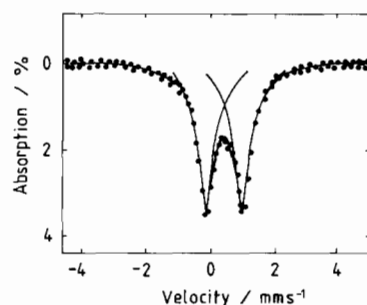

Fig. 4. Mössbauer spectrum of Fe(mepheo-a)(py)₂ at 77 K.

TABLE 3. Mössbauer parameters for Fe(mepheo-a)(4-Xpy)₂^a and low-spin iron(II) porphyrins^b (77 K)

No.	Compound	δ (mm s^{-1})	ΔE_q (mm s^{-1})
1	Fe(mepheo-a)(py)₂	0.44(5)	1.11(6)
2	Fe(mepheo-a)(4-CH₃py)₂	0.42(4)	1.30(7)
3	Fe(mepheo-a)(4-COCH₃py)₂	0.42(0)	1.28(7)
4	Fe(mepheo-a)(4-COOCH₃py)₂	0.39(9)	1.27(6)
5	Fe(mepheo-a)(4-Clpy)₂	0.39(6)	0.93(4)
6	Fe(mepheo-a)(4-CNpy)₂	0.37(9)	0.94(1)
	Fe(pp)(py)₂	0.45	1.21
	Fe(oep)(py)₂	0.46	1.14
	Fe(tpp)(py)₂	0.40	1.15

^{a}Estimated uncertainties were ±0.008 mm s^{-1}. ^{b}Taken from ref. 1. Porphyrin abbreviations are the same as those in Table 1.
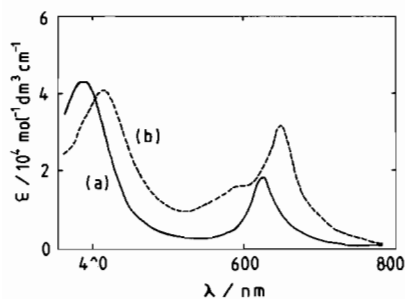
Fig. 5. Spectral change of Fe(mepheo-a)Cl before (a) and after (b) treatment with pyridine.

with that by method II. This fact also supports the autoreduction by heating with pyridine.

Bonding properties of Fe(mepheo-a)(4-Xpy)₂

The Mössbauer parameters of Fe(mepheo-a)(4-Xpy)$_2$ are listed in Table 3. These parameters indicate that the high-spin iron(III) ion in Fe(mepheo-a)Cl is autoreduced to the low-spin iron(II) ion by the coordination of the pyridine derivatives as well as pyridine. The autoreduction was also confirmed by the fact that the products obtained by method I and those by method II give the same electronic spectra. In the low-spin iron(II) complexes, the bonding between the iron and the axial ligands consists of σ-donation and π-backdonation. The former is the electron donation from the filled σ-orbitals of the axial ligand to the unfilled orbitals of the iron ion. The latter is the electron donation from the iron d_π (d_{xz}, d_{yz}) orbitals to the unfilled π^* orbitals of the axial ligand. The increased σ-donation enhances the iron 4s population. The increased π-backdonation decreases the iron d_π population, which causes decreased shielding. Hence, the isomer shift is lowered with both increased σ-donation and π-backdonation. For the quadrupole splitting, the electric-field gradient (EFG) is responsible for the valence contribution (q_{val}), i.e. an imbalance of the electron population in the iron 3d orbitals because the lattice contribution is very small in the present case. The q_{val} is expressed in terms of the 3d population (n_i) as follows [24]

$$q_{val} = 4/7(1-R)\langle r^{-3}\rangle [n_{x^2y^2} + n_{xy} - n_{z^2} - 1/2(n_{xz} + n_{yz})]$$

$$(q_{val} > 0)$$

where R is Sternheimer antishielding factor, $\langle r^{-3}\rangle$ is the expectation value for r^{-3} (r: radial part of 3d wave function). The increased σ-donation of the axial ligands enhances the n_z population, and the increased π-backdonation decreases the n_{xz} and n_{yz} populations. Therefore, the isomer shift decreases with decreasing quadrupole splitting if the σ-donation is predominant. On the other hand, the isomer shift decreases with increasing quadrupole splitting if the π-backdonation is

predominant. In the present case the quadrupole splitting tends to increase with the isomer shift, indicating that the σ-donation is predominant in the axial bonding.

The isomer shifts are plotted against Hammett's constants (σ_p) [25], which are parameters of the electron-withdrawing ability of the substituents, in Fig. 6. The correlation with a negative slope indicates that the smaller the isomer shift, the stronger the electron-withdrawing of the substituent at the 4-position of pyridine. Taking the predominance of the σ-donation into consideration, the correlation observed here is ascribed to the increasing σ-donation caused by the synergetically increased π-backdonation. Thus, the π-backdonation also plays some role in the axial bonding. The synergetic effect between the σ-donation and π-backdonation is supported by the relationship between the isomer shifts and the pK_a of the free ligands [26]. If the synergetic effect is absent, the axial ligand with larger pK_a should lead to a smaller isomer shift because of the increased 4s population. Hence the correlation with a positive slope shown in Fig. 7 implies that the stronger the π-backdonation, the stronger the σ-donation. The absorptions, Soret band and Q band, reflect the $\pi-\pi^*$ excitations on the chlorin ring. The isomer

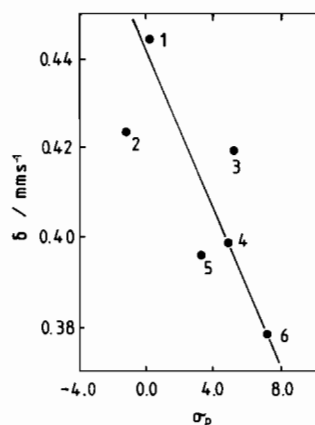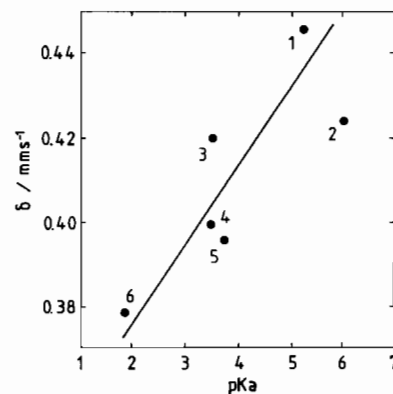Fig. 6. Plots of δ against σ_p.

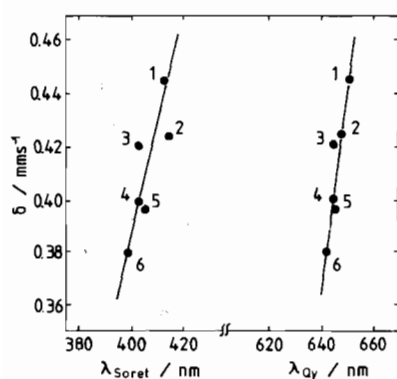Fig. 7. Relationship between δ and pK_a of the free ligand.

Fig. 8. Plots of δ vs. λ_{Soret} and σ vs. λ_{Qy}.

shifts are plotted against the absorption wavelengths of the Soret and Q bands of Fe(mepheo-a)(4-Xpy)$_2$ in Fig. 8. The correlation with a positive slope indicates that the difference in the π-backdonation to the axial ligands affects the π--π^* excitations of the chlorin ring via the central iron d_π orbitals.

Acknowledgement

References

1 J. R. Sams and T. B. Twin, in D. Dolphin (ed.), *The Porphyrins,* Vol. IV, Academic Press, New York, 1979, Ch. 9.

2 F. Adar, in D. Dolphin (ed.), *The Porphyrins,* Vol. III, Academic Press, New York, 1978, Ch. 2.

3 A. M. Stolzenberg, S. H. Strauss and R. H. Holm, *J. Am. Chem. Soc., 103* (1981) 4763.

4 S. H. Strauss, M. J. Pawlik, J. Skowya, J. R. Kennedy, O. P. Anderson, K. Spartalian and J. L. Dye, *Inorg. Chem., 26* (1987) 724.

5 S. H. Strauss, M. E. Silver, K. M. Long, R. G. Thompson, R. A. Hudgens, K. Spartalian and J. A. Ibers, *J. Am. Chem. Soc., 107* (1985) 4207.

6 Y. Ozaki, K. Iriyama, H. Ogoshi, T. Ochiai and T. Kitagawa, *J. Phys. Chem., 90* (1986) 6105.

7 N. J. Boldt and D. F. Bocian, *J. Phys. Chem., 92* (1988) 581.

8 H. Hori, K. Kadono, H. Inoue, T. Shirai and E. Fluck, *J. Radioanal. Nucl. Chem. Lett., 136* (1989) 159.

9 H. Hori, K. Kadono, K. Fukuda, H. Inoue, T. Shirai and E. Fluck, *J. Radioanal. Nucl. Chem. Lett., 137* (1989) 277.

10 H. Hori, K. Kadono, K. Fukuda, H. Inoue, T. Shirai and E. Fluck, *Radiochim. Acta, 49* (1990) 77.

11 D. Jerchel, H. Fischer and K. Thomas, *Chem. Ber., 89* (1956) 2921.

12 F. C. Pennington, H. H. Strain, W. A. Svec and J. J. Katz, *J. Am. Chem. Soc., 86* (1964) 1418.

13 M. Blume, *Phys. Rev. Lett., 18* (1967) 305.

14 C. Bartocci, M. Maldotti, O. Traverso, C. A. Bignozzi and V. Carassiti, *Polyhedron, 2* (1983) 97.

15 C. Bartocci, F. Scandola, A. Ferri and V. Carassiti, *J. Am. Chem. Soc., 102* (1980) 7067.

16 A. Maldotti, C. Bartocci, C. Chiorboli, A. Ferri and V. Carassiti, *J. Chem. Soc., Chem. Commun.,* (1985) 881.

17 G. S. Srivatsa and D. T. Sawyer, *Inorg. Chem., 24* (1985) 1732.

18 L. B. Dugad, O. K. Medhi and S. Mitra, *Inorg. Chem., 26* (1987) 1741.

19 S. Mazumdar, L. B. Dugad, O. K. Medhi and S. Mitra, *J. Chem. Soc., Dalton Trans.,* (1988) 2797.

20 L. M. Epstein, D. K. Straub and C. Maricondi, *Inorg. Chem., 6* (1967) 1720.

21 J. A. Weightman, N. J. Hoyle and R. J. P. Williams, *Biochim. Biophys. Acta, 244* (1971) 567.

22 P. H. Hynninen and S. Lotjonen, *Synthesis,* (1983) 705.

23 T. Watanabe, M. Nakazato, M. Konno, S. Saitoh and K. Honda, *Chem. Lett.,* (1984) 1411.

24 F. Calderazzo, S. Frediani, B. R. James, G. Pampaloni, K. J. Reimer, J. R. Sams, A. M. Serra and D. Vitali, *Inorg. Chem., 21* (1982) 2302.

25 N. Inamoto, *Hammett Soku,* Maruzen, Tokyo, 1983.

26 A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.,* (1964) 3591.