BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1471—1479 (1973)

Electronic Spectra of High-Spin Iron(III) Tetraphenylporphins

Hiroshi KOBAYASHI, Yasuo YANAGAWA, Hisajiro OSADA,
Shuji MINAMI, and Masayuki SHIMIZU

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received September 16, 1972)

Characterization of the electronic absorption spectra of high-spin iron(III) porphyrins was carried out on the basis of observation and theoretical calculation for tetraphenylporphinatoiron(III) and -manganese(III) complexes.

Electronic absorption spectra of the iron(III) porphyrins have not been wholly understood, although experimental correlations between the electronic structure and spectra have been studied mainly for analysis of their behaviors in the biological processes. Many physico-chemical studies have been carried out on the ferri-hemoproteins occurring in nature such as methemoglobin, catalase, peroxidase, and cytochromes.[1] We present in this paper a characterization of the electronic absorption spectra of high-spin iron(III) porphyrins on the basis of observation and theoretical calculation for tetraphenylporphinatoiron(III) and -manganese(III) complexes.

Experimental

Synthesis of the Metal-free Base of Tetraphenylporphin. $\alpha,\beta,\gamma,\delta$-Tetraphenylporphin (TPP) was synthesized from pyrrole and benzaldehyde by the method of Adler *et al.*[2] Methods developed by Rothermund and by others[3] were also used in preliminary experiments. TPP was precipitated from chloroform elute of the product by adding excess methanol. The crystals thus obtained were recrystallized from chloroform-methanol mixture. Chromatographic purification was repeated on activated alumina columns using chloroform as solvent and also eluent. After the eluate was concentrated, excess methanol was added. Purple needle crystals thus obtained were identified by elemental analysis.

Found: C, 86.02; H, 5.18; N, 8.94%. Calcd for $C_{44}H_{30}N_4$: C, 85.97; H, 4.92; N, 9.11%.

The electronic absorption spectrum of the product dissolved in benzene was in excellent agreement with reported spectra.[4-6]

Syntheses of Tetraphenylporphinatoiron(III) Complexes. The methods of Rothermund and Menotti[7] and Dorough *et al.*[8] were employed with some modification. About 500 mg of the metal-free base and 300 mg sodium chloride were dissolved in 50 ml chloroform. A saturated solution of ferrous acetate in acetic acid, prepared just before use by dissolving iron powder in 150 ml glacial acetic acid while still warm, was added to a chloroform solution of TPP. The mixture was refluxed for 3 hr and then most of the chloroform and acetic acid was distilled off. When the solution was concentrated up to 50 ml, TPPFe(III)Cl was precipitated by adding methanol. The crystals thus obtained were repeatedly recrystallized from the mixed solvent chloroform-methanol. The recrystallized blue violet needle crystals were identified

1) See, for example, J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., Amsterdam (1964); J. E. Falk, R. Lemberg and R. K. Morton, "Haematin Enzymes," Pergamon Press, Oxford (1961); B. Chance, R. W. Estabrook and T. Yonetani, "Hemes and Hemoproteins," Academic Press, New York (1966).

2) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

3) P. Rothermund, *J. Amer. Chem. Soc.*, **59**, 2010 (1935); P. Rothermund and A. R. Menotti, *ibid.*, **63**, 267 (1941); S. Aronoff and M. Calvin, *J. Org. Chem.*, **8**, 205 (1934); R. H. Ball, G. D. Dorough and, M. Calvin, *J. Amer. Chem. Soc.*, **68**, 2278 (1946).

4) D. W. Thomas and A. E. Martell, *J. Amer. Chem. Soc.*, **78**, 1335, 1338 (1956).

5) G. M. Badger, R. A. Jones, and R. L. Laslett, *Austral. J. Chem.*, **17**, 1028 (1964).

6) J. Mullins, A. D. Adler, and R. Hochstrasser, *J. Chem. Phys.*, **43**, 2548 (1965).

7) P. Rothermund and A. R. Menotti, *J. Amer. Chem. Soc.*, **70**, 1808 (1948).

8) G. P. Dorough, J. R. Miller, and F. M. Huennekens, *ibid.*, **73**, 4315 (1951).

TABLE 1. ELEMENTAL ANALYSES

TPPFe(III)X	Found (%)				Calcd (%)			
	C	H	N	Fe	C	H	N	Fe
$C_{44}H_{28}N_4FeBr$	71.27	3.89	7.51	7.32	70.61	3.77	7.49	7.46
$C_{44}H_{28}N_4FeI$	68.19	3.70	7.36	7.15	66.44	3.55	7.04	7.02
$C_{44}H_{28}N_4FeSCN$	73.39	3.86	9.36	7.72	74.38	3.88	9.64	7.69
$C_{44}H_{28}N_4FeOCOCH_3$	75.13	4.23	7.47	7.70	75.93	4.39	7.70	7.68

by elemental analysis.

Found: C, 74.81; H, 4.11; N, 7.76; Fe, 7.82%. Calcd for $C_{44}H_{28}N_4FeCl$: C, 75.07; H, 4.01; N, 7.96; Fe, 7.93%.

Iron was determined by colorimetry using phenanthroline.

TPPFe(III)Br, TPPFe(III)I, TPPFe(III)SCN, and TPPFe(III)$OCOCH_3$ were synthesized and purified by similar methods to those for TPPFe(III)Cl. The products were identified by elemental analyses (Table 1).

Synthesis of Tetraphenylporphinatomanganese(III) Chloride. TPPMn(III)Cl·H_2O was prepared by the method of Rothermund and Menotti.[7] The metal-free base and manganese(II) acetate were refluxed in a mixed solvent chloroform-acetic acid. Recrystallization from mixed solvent dry chloroform-ligroin gave green crystals. The absorption spectrum of the complex dissolved in pyridine was in good agreement with that in the literature.[9]

Found: C, 74.85; H, 4.30; N, 8.18; Mn, 7.67%. Calcd for $C_{44}H_{28}N_4MnCl\cdot H_2O$: C, 73.28; H, 4.19; N, 7.77; Mn, 7.62%.

Manganese was determined by colorimetry after it had been oxidized to permanganate.

Measurements of Absorption Spectra and Magnetic Circular Dichroism. Electronic absorption spectra were recorded on a Shimadzu recording spectrophotometer Model MPS-50 and a Beckman DU spectrophotometer using quartz cells of 0.1 and 1.0 cm light path. Solvents were benzene, methanol and pyridine purified by fractional distillations using a 1.5 m wire packed column and dried by the usual procedures.[10]

The absorption spectra of powder samples were measured by the opal glass method.[11] Instead of an opal glass plate, we placed a sheet of tracing paper smeared with the solid sample in front of the window of an end-on type photomultiplier in the Shimadzu spectrophotometer. The absorption spectra thus obtained were better than those observed by the original opal glass method.

Circular dichroism under an external magnetic field (MCD) was measured by a JASCO automatic recording spectropolarimeter Model ORD/UV-5 with CD attachment and an electromagnet.[12] The magnetic field was set at 10000 Gauss.

Magnetic Susceptibility. Magnetic susceptibilities of the complexes were measured at room temperature by means of the Gouy method. After calibrating for the diamagnetic term by the usual method,[13] the magnetic moment of complexes was evaluated. The magnetic moment in solution was also determined by the same method.

TABLE 2. MAGNETIC MOMENTS OF IRON(III)- AND MANGANESE (III) TETRAPHENYLPORPHINS

Complex	Magnetic moment (Bohr magneton)	Number of unpaired electrons	Spin state
TPPFe(III)Cl	5.88	5	$S=5/2$
TPPFe(III)Br	6.08	5	$S=5/2$
TPPFe(III)I	5.71	5	$S=5/2$
TPPFe(III)SCN	5.75	5	$S=5/2$
TPPFe(III)$OCOCH_3$	6.03	5	$S=5/2$
TPPFe(III)Cl in chloroform	5.6	5	$S=5/2$
TPPMn(III)Cl·H_2O	4.98	4	$S=2$

Results and Discussion

Iron(III) porphins with an ionic axial ligand such as Cl^-, Br^-, I^-, SCN^-, CH_3COO^- are in the high-spin state $S=5/2$. The spin state of TPPFe(III)X was identified by magnetic susceptibility measurements. The results are summarized in Table 2. These high-spin TPPFe(III)X complexes with different axial ligands actually gave the same absorption spectrum in shape and position. A typical absorption spectrum of TPPFe(III)X ($S=5/2$) in benzene is shown in Fig. 1. The spectrum has a more complicated profile as compared with the typical absorption spectra obtained for the lowest (π, π^*) transitions of the square planar metal porphins. Figure 1 also shows characteristic

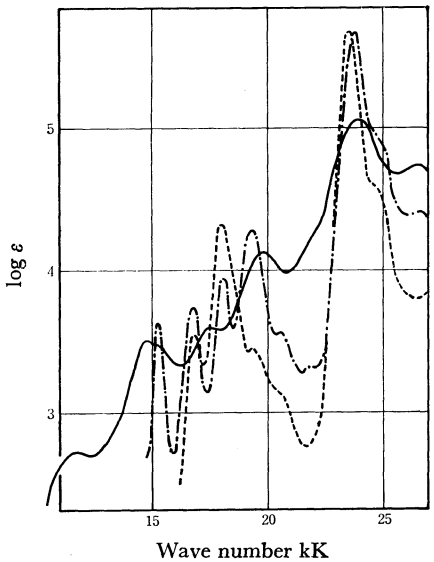

Fig. 1. Absorption spectra of TPPFe(III)Cl, TPPZn(II) and the metal free base in benzene.
——: TPPFe(III)Cl – – –: TPPZn(II)
–·–·–: $TPPH_2$

9) L. J. Boucher, *ibid.*, **92**, 2725 (1970).

10) J. A. Riddick and E. E. Troops, "Organic Solvents, Techniques of Organic Chemistry," Vol. 7, ed. by A. Weissberger, Interscience Publishers, New York (1955).

11) K. Shibata, "Methods of Biochemical Analysis," Vol. 7, ed. by D. Glick, Intersciences Publishers, New York (1959), p. 77.

12) H. Kobayashi, M. Shimizu, and I. Fujita, This Bulletin, **43**, 2335 (1970).

13) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," ed. by J. Lewis and R. G. Wilkins, Interscience Publishers, New York (1960), p. 415.

absorption spectra of the metal-free porphin (D_{2h}) and square planar metal porphins (D_{4h}).

The general feature of the absorption spectrum of TPPFe(III)X is in good agreement with that of a characteristic absorption spectrum of the high-spin species of ferri-hemoproteins. George, Beetlestone and Griffith separated high- and low-spin spectral types for the ferri-hemoproteins by combining spectroscopic and magnetic data,[14] and showed that in the case of ferri-hemoproteins, the iron(III) porphyrin is in an equilibrium between two spin states $S=5/2$ and $S=1/2$. They were able to get limiting spectra from the mixture spectra of two spin states. Although the existence of negative absorption regions shows some deficiency in their assumptions, the overall results seem to be sound.

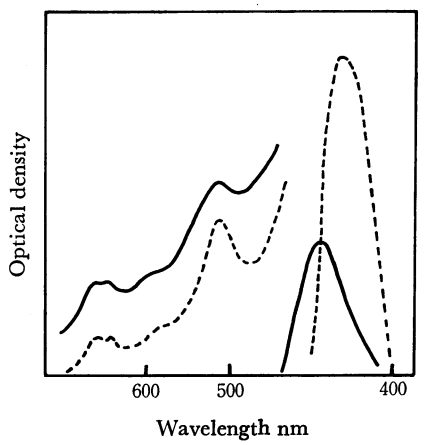

Fig. 2. Absorption spectrum of TPPFe(III)Cl in the solid state.
——: powder – – –: benzene solution

The magnetic susceptibility measurement of TPPFe(III)Cl in chloroform solution indicates that the spin state found in the solid state is well preserved in chloroform solution. Chloroform was used instead of benzene because of the higher solubility of porphin. The absorption spectrum of TPPFe(III)Cl in chloroform was coincident with that of the benzene solution. In contrast, the solid state absorption spectrum of TPPFe(III)Cl obtained by the modified opal glass method was in good agreement with that of the benzene solution except for a red shift of the Soret band in the solid state which might be due to an exciton coupling between the strong Soret oscillators packed in a molecular crystal (Fig. 2). The spin state of the complex TPPFe(III)Cl does not change upon dissolution. Thus such a complicated spectrum as shown in Fig. 1 should be assigned to the absorption spectrum characteristic of high-spin iron(III) porphin.

The lowest excitations in a typical D_{4h} metal porphin are assigned to the lowest (π, π^*) transitions approximately described by a 50-50 admixture of the transitions $(3a_2)\rightarrow(4e)$ and $(1a_1)\rightarrow(4e)$, where $(3a_2)$ and $(1a_1)$ are the highest occupied orbitals and (4e) the degenerate lowest vacant orbitals. A configuration interaction between these two excited configurations

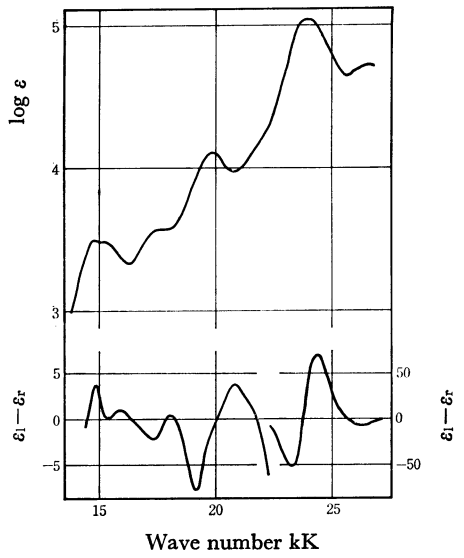

Fig. 3. MCD spectrum of TPPFe(III)Cl in benzene.
Upper: absorption spectrum Lower: MCD spectrum

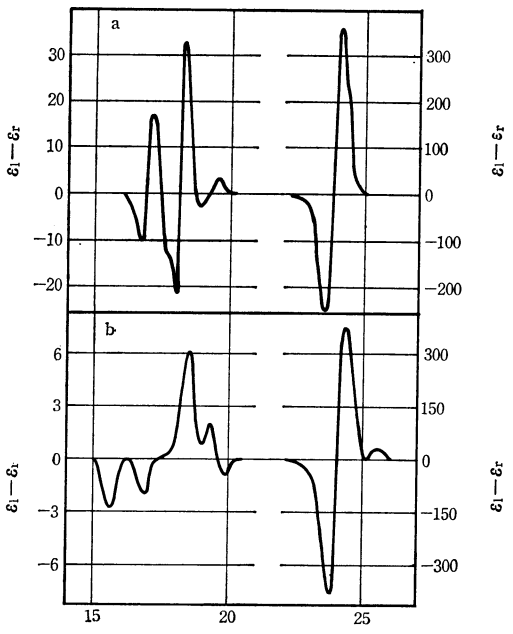

Fig. 4. MCD spectra of TPPZn(II) and the metal free base in benzene.
a: TPPZn(II), b: $TPPH_2$

gives rise to the lowest transition of forbidden character and the second lowest transition of allowed character, the former being Q transition and the latter B transition (or Soret transition). This is a four-orbital description of the lowest (π, π^*) transition in porphin.[15] The lowest electronic excitations of TPPZn(II), in which only a very small π interaction between metal and porphin is present, are well described by the four-orbital model.[16,17] However, the model can not ex-

14) P. George, J. Beetlestone, and J. S. Griffith, "Haematin Enzymes," ed. by J. E. Falk, R. Lemberg, and R. K. Morton, Pergamon Press, Oxford (1961), p. 105.

15) M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959).
16) H. Kobayashi, *ibid.*, **30**, 1362 (1959).
17) C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectrosc.*, **16**, 415 (1965).

plain the lowest excitations of high-spin TPPFe(III)X complexes. A similarity in the visible absorption spectra of high-spin iron(III) porphin and the metal-free base has been pointed out.[18] However, these two porphins show quite different MCD spectra as shown in Figs. 3 and 4. The visible and near-ultraviolet absorption spectra of the metal-free base are described as the lowest (π, π^*) transitions. Thus the splitting of the visible Q band was, in principle, well reproduced by a Pariser-Parr-Pople molecular orbital calculation.[17]

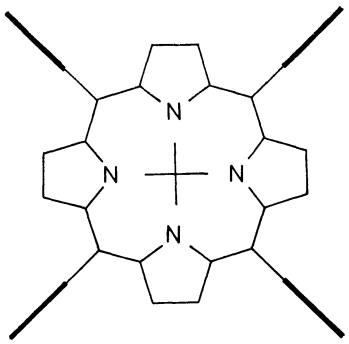

Fig. 5. Molecular geometry of metal tetraphenylporphin. Phenyl groups are actually perpendicular to the molecular plane of porphin.

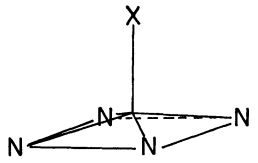

Fig. 6, The coordination sphere of iron(III) ion in TPPFe(III)X. Iron ion is slightly out of the porphin plane.

Tetraphenylporphin has a planar structure as shown in Fig. 5. The central iron is displaced out-of-plane from the nitrogen atoms by 0.4 Å as found by X-ray crystallographical studies on various metal porphyrins including metal tetraphenylporphins.[19,19a] The structure of the coordination sphere of iron(III) ion in TPPFe(III)X is schematically shown in Fig. 6. A simple argument in terms of the angular-overlap model predicts the ordering of d orbitals in a planar ligand field of porphin:[20]

$$\varepsilon(x^2-y^2) = \Delta,\ \varepsilon(z^2) = \Delta/3,\ \varepsilon(xy) = \varepsilon(yz) = \varepsilon(zx) = 0,$$

where Δ is the ligand field splitting parameter. Since a mixing between z^2 and s orbitals is crucial in a planar environment, $\varepsilon(z^2)$ is much lower than that predicted from the angular-overlap model and is, in fact, close to zero. The energy difference $\varepsilon(x^2-y^2)-\varepsilon(z^2)$ varies with the axial ligand field and can be parametrized as $x\Delta$. The energy of the possible ground configurations of TPPFe(III)X is approximately given as follows:

$$\begin{aligned}
&^6A_1\ [(xy)(yz)(zx)(z^2)(x^2-y^2)] && (2-x)\Delta - 35B,\\
&^4A_2\ [(xy)^2(yz)(zx)(z^2)] && (1-x)\Delta - B,\\
&^2E\ \ [(xy)^2(zx)^2(yz)] && \\
&\quad\ [(xy)^2(yz)^2(zx)] && 20B,
\end{aligned}$$

where B is Racah's electrostatic interaction parameter (assumed $C=4B$). The energy diagram of the ground configuration is given in Fig. 7. The value of Δ in porphin has been evaluated 25—31B by an extended Hückel molecular orbital calculation.[21] The value was consistent with the observations on tetraphenylporphinatoiron(II) complexes.[20] As Fig. 7 shows, the

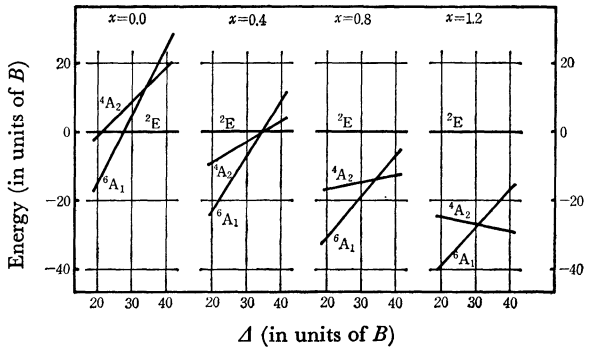

Fig. 7. Energy diagrams of the ground state of iron(III) ion in TPPFe(III)X. Δ is the ligand field splitting parameter in units of B and $x\Delta(\varepsilon(x^2-y^2)-\varepsilon(z^2))$, the axial ligand field parameter.

most stable ground configuration for Δ=25—31B is ^{6}A if the axial ligand field is not so strong. Since the axial ligand field of the complexes studied is as weak as x=0.4—1.0, the ground configuration is ^{6}A and all the five d orbitals are singly occupied. Thus the spin-allowed excited states should be sextet. The charge-transfer excitations of an electron in the highest filled porphin π orbitals to the half-filled d_{zx} and d_{yz} orbitals (dπ orbitals) give rise to degenerate excited states of E symmetry. Since iron dπ orbitals and the lowest vacant orbitals 4e of porphin are of the same centrosymmetry, an electronic delocalization between these orbitals appreciably occurs when they are energetically close. Thus the lowest excited sextets of E symmetry should be described by a superposition of the antisymmetric product wavefunctions ^{6}E[^{3}E($1a_1\rightarrow 4e$)·^{6}A], ^{6}E[^{3}E($3a_2\rightarrow 4e$)·^{6}A], ^{6}E[^{1}E($1a_1\rightarrow 4e$)·^{6}A], ^{6}E[^{1}E($3a_2\rightarrow 4e$)·^{6}A], ^{6}E[$^2A_1(1a_1)$·^{5}E(dπ)], and ^{6}E[$^2A_2(3a_2)$·^{5}E(dπ)],

18) W. Scheler, G. Schoffa, and H. Jung, *Biochem. Z.*, **329**, 232 (1957); W. Scheler, *ibid.*, **332**, 344, 542 (1960).

19) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967).

19a) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, **87**, 2312 (1965); D. F. Koenig, *Acta Crystallogr.*, **18**, 663 (1965); J. L. Hoard, "Hemes and Hemoproteins," ed. by B. Chance, R. W. Estabrook, and T. Yonetani, Academic Press, New York (1966), p. 9; D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2006 (1972); L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2073 (1972); A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *ibid.*, **94**, 3620 (1972); J. C. Kendrew, *Science*, **139**, 1259 (1963); M. F. Perutz, *ibid.*, **140**, 863 (1963); M. F. Perutz, H. Muirhead, J. M. Cox, and L. C. G. Goaman, *Nature*, **219**, 131 (1968).

20) H. Kobayashi, and Y. Yanagawa, This Bulletin, **45**, 450 (1972).

21) M. Zerner, M. Gouterman, and H. Kobayashi, *Theoret. Chim. Acta*, **6**, 363 (1966).

where $^3E(1a_1\rightarrow 4e)$, $^3E(3a_2\rightarrow 4e)$, $^1E(1a_1\rightarrow 4e)$, and $^1E(3a_2\rightarrow 4e)$ denote the wavefunctions of the lowest porphin-localized triplet and singlet excited states, respectively, ^6A denotes the ground iron(III) sextet state, and $^6E[^2A_1(1a_1)\cdot{}^5E(d\pi)]$ and $^6E[^2A_2(3a_2)\cdot{}^5E(d\pi)]$ the excited state arising from the "porphin to iron(III) ion" charge-transfers $1a_1\rightarrow d\pi$ and $3a_2\rightarrow d\pi$, respectively. Delocalization between the orbitals $d\pi$ and 4e connects two states that differ by a single orbital, as in $^6E[^{1,3}E(1a_1\rightarrow 4e)\cdot{}^6A]$ and $^6E[^2A_1(1a_1)\cdot{}^5E(d\pi)]$, $^6E[^{1,3}E(3a_2\rightarrow 4e)\cdot{}^6A]$ and $^6E[^2A_2(3a_2)\cdot{}^5E(d\pi)]$.

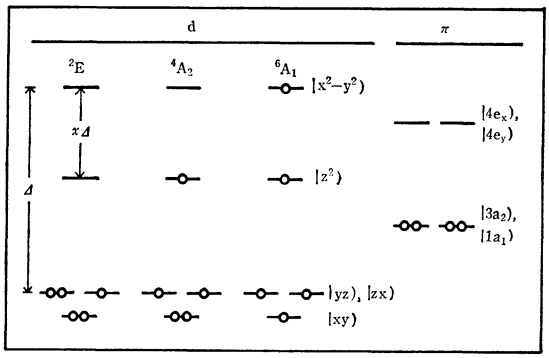

Fig. 8. Energy levels of the top filled and the lowest vacant orbitals (schematic).

The energies of the charge-transfers from $1a_1$, $3a_2$ to $d\pi$ are not as low as expected from the orbital energy diagrams shown in Fig. 8, since the charge-transfer needs an extra work done for a change of the electrostatic potential term. When an electron makes a transfer from the conjugation circuit of porphin with radius R to the central iron(III) ion, the extra work done against a change in the electrostatic potential is approximately given e^2/R assuming a neutral charge distribution in the ground state. The radius R of the main conjugation circuit of porphin is estimated to be 3.3 Å from the X-ray data. Thus e^2/R is evaluated to be 4.4 eV.[19]

The energies of the lowest excitations localized in porphin are given as follows. For the transition $1a_1\rightarrow 4e$,

$$\varepsilon(4e)-\varepsilon(1a_1)-(a_1a_1|ee)+\binom{2}{0}(a_1e|a_1e)$$

and for the transition $3a_2\rightarrow 4e$,

$$\varepsilon(4e)-\varepsilon(3a_2)-(a_2a_2|ee)+\binom{2}{0}(a_2e|a_2e)$$

where ε denotes molecular orbital energy, $(a_1a_1|ee)$ and $(a_1a_1|ee)$ denote the Coulomb integrals over the molecular orbitals, $1a_1$, $3a_2$, and 4e, $(a_1e|a_1e)$ and $(a_2e|a_2e)$, the exchange integrals, and the upper integer of $\binom{2}{0}$ denotes the coefficient for the singlet and the lower one for the triplet. Gouterman has pointed out an accidental degeneracy of the top filled orbitals on the basis of the observed substituent effects of the singlet-singlet absorption spectra of porphins.[15] Strictly speaking, it is an accidental degeneracy of the lowest excited singlet configurations rather than one of the top filled orbitals:

$$\varepsilon(4e)-\varepsilon(1a_1)-(a_1a_1|ee)+2(a_1e|a_1e)$$
$$\fallingdotseq\varepsilon(4e)-\varepsilon(3a_2)-(a_2a_2|ee)+2(a_2e|a_2e).$$

Experimental evidences show that the excited singlet configuration $(1a_1)(4e)$ is slightly lower than the excited singlet configuration $(3a_2)(4e)$. The energies of these configurations are given by $(E+2K)\pm(E'+2K')$, where $E\equiv\varepsilon(4e)-\{\varepsilon(3a_2)+\varepsilon(1a_1)\}/2-\{(a_2a_2|ee)+(a_1a_1|ee)\}/2$, $E'\equiv\{\varepsilon(1a_1)-\varepsilon(3a_2)\}/2+\{(a_1a_1|ee)-(a_2a_2|ee)\}/2$, $K\equiv\{(a_2e|a_2e)+(a_1e|a_1e)\}/2$, and $K'\equiv\{(a_2e|a_2e)-(a_1e|a_1e)\}/2$. The energies of the lowest excited singlets are given by $(E+2K)\pm\sqrt{(E'+2K')^2+(2K'')^2}$, where $2K''$ denotes configuration interaction matrix $2(a_1e|a_2e)$. Gouterman's finding that $E'+2K'\fallingdotseq 0$ does not necessarily imply an accidental degeneracy of the lowest triplets. The energies of the lowest triplets are given by $E\pm E'\fallingdotseq E\mp 2K'$. As experimental evidences show, $E'+2K'\equiv\varepsilon$ is small but positive. Thus the triplet $(3a_2)(4e)$ is lower than the triplet $(1a_1)(4e)$ when $2K'>\varepsilon$, but higher when $2K'<\varepsilon$. A Pariser-Parr-Pople SCMO calculation has revealed that $\varepsilon\fallingdotseq 0$, $2K'>\varepsilon$ and $\varepsilon(1a_1)\fallingdotseq\varepsilon(3a_2)$. Thus the lowest triplet is much likely to be $(3a_2)(4e)$, although it was recently assigned to the triplet $(1a_1)(4e)$ because of no nitrogen hyperfine structure being observed in the ESR spectrum of the lowest triplet of zinc(II) porphin.[22] The orbital $(1a_1)$, in fact, lacks populations on the central nitrogens, whereas the orbital (4e) has populations on the nitrogens as well as $(3a_2)$. No further evidences to support the lowest triplet $(1a_1)(4e)$ have been presented.

A circular box is described by a radial coordinate r and angular coordinate θ. Orbitals are written $|\pm k)=f(r)\exp(\pm ik\theta)$, where k denotes orbital angular momentum. The orbital pair $(3a_2\pm i1a_1)/\sqrt{2}$ can be identified with the degenerate pair of circular box orbitals $|\pm 4)=f(r)\exp(\pm 4i\theta)$, and the lowest empty 4e orbitals $|\pm 5)=f(r)\exp(\pm 5i\theta)$.[23] In the ground state, a pair of orbitals which has z components of angular momentum $\lambda_z=\pm 4$ and angular momentum $\lambda=4$ is filled with four electrons; the ground configuration is denoted $(4)^4$ and has zero angular momentum $A_z=0$. The first excited configurations arise by exciting a $\lambda=4$ electron to an orbital with $\lambda=5$, and are denoted $(4)^35$. The configurations give rise to degenerate pairs of excited states with $A_z=\pm 1$ and $A_z=\pm 9$.

A degenerate $d\pi$ orbital pair, zx and yz, causes a charge-transfer interaction with the porphin π molecular orbitals of E symmetry. The orbital pair can be rewritten $|\pm 1)=(zx\pm iyz)/\sqrt{2}$, where ± 1 denotes the z components of angular momentum $\lambda=1$. A one-electron term connecting the orbitals $|\pm 1)$ and $|\pm 5)$, $(\pm 1|h^{\text{eff}}|\pm 5)\equiv\beta$, gives rise to a delocalization of the porphin π electrons toward the half-filled iron(III) $d\pi$ orbitals.

The electrons in the orbitals with $\lambda=1$, $\lambda=4$, and $\lambda=5$ are assumed to move in a one-electron effective core field set up by the nuclei and the remaining electrons and to interact with one another by the two-

22) I. Y. Chan, W. G. van Dorp, T. J. Schaafsma, and J. H. van der Waals, *Mol. Phys.*, **22**, 741 (1971).
23) M. Gouterman, *J. Chem. Phys.*, **33**, 1523 (1960).

TABLE 3. GROUND AND EXCITED SEXTETS OF HIGH-SPIN IRON(III) PORPHIN

State	Configuration	Λ_z	$2S+1$	Energy
^6A	$\varepsilon\theta\zeta(+1)(-1)(+4)^2(-4)^2$	0	6	0
$^6E_{CT}$	$\varepsilon\theta\zeta(+1)^2(-1)(+4)^2(-4)$	+5	6	E_{CT}
	$\varepsilon\theta\zeta(+1)(-1)^2(+4)(-4)^2$	−5	6	E_{CT}
$^6E_{CT}$	$\varepsilon\theta\zeta(+1)^2(-1)(+4)(-4)^2$	−3	6	E_{CT}
	$\varepsilon\theta\zeta(+1)(-1)^2(+4)^2(-4)$	+3	6	E_{CT}
^6E_T	$\varepsilon\theta\zeta(+1)(-1)(+4)^2(-4)(+5)$	+9	6	E
	$\varepsilon\theta\zeta(+1)(-1)(+4)(-4)^2(-5)$	−9	6	E
^6E_T	$\varepsilon\theta\zeta(+1)(-1)(+4)(-4)^2(+5)$	+1	6	E
	$\varepsilon\theta\zeta(+1)(-1)(+4)^2(-4)(-5)$	−1	6	E
^6E_Q	$\varepsilon\theta\zeta(+1)(-1)(+4)^2(-4)(+5)$	+9	6	$E+2K_9$
	$\varepsilon\theta\zeta(+1)(-1)(+4)(-4)^2(-5)$	−9	6	$E+2K_9$
^6E_B	$\varepsilon\theta\zeta(+1)(-1)(+4)(-4)^2(+5)$	+1	6	$E+2K_1$
	$\varepsilon\theta\zeta(+1)(-1)(+4)_2(-4)(-5)$	−1	6	$E+2K_1$

Mixing terms for high-spin iron(III) porphin

	$^6E_{CT}$	$^6E_{CT}$	^6E_T	^6E_T	^6E_Q	^6E_B
$^6E_{CT}$	E_{CT}	ε''	$\frac{\sqrt{70}}{10}\beta$	0	$\frac{\sqrt{2}}{2}\beta$	0
$^6E_{CT}$		E_{CT}	0	$\frac{\sqrt{70}}{10}\beta$	0	$\frac{\sqrt{2}}{2}\beta$
^6E_T			E	ε'	0	0
^6E_T				E	0	0
^6E_Q					$E+2K_9$	ε
^6E_B						$E+2K_1$

Mixing terms for high-spin manganese(III) porphin

	$^5E_{CT}$	$^5E_{CT}$	^5E_T	^5E_T	^5E_Q	^5E_B
$^5E_{CT}$	E_{CT}	ε''	$\frac{\sqrt{3}}{2}$	0	$\frac{\sqrt{2}}{2}\beta$	0
$^5E_{CT}$		E_{CT}	0	$\frac{\sqrt{3}}{2}\beta$	0	$\frac{\sqrt{2}}{2}\beta$
^5E_T			E	ε'	0	0
^5E_T				E	0	0
^5E_Q					$E+2K_9$	ε
^5E_B						$E+2K_1$

electron term e^2/r_{ij}. Wavefunctions are taken as Slater determinants which are eigenfunctions of total spin sextet. In Table 3 are given the sextet states arising from the configurations $\varepsilon\theta\zeta(1)^2(4)^4$, $\varepsilon\theta\zeta(1)^3(4)^3$, and $\varepsilon\theta\zeta(1)^2(4)^3(5)$, ε denoting iron x^2-y^2 orbital, θ, z^2 orbital and ζ, xy orbital, respectively. Slater determinants are then taken as follows:

$$|+5\rangle \equiv |\varepsilon\theta\zeta+1-1+4+\bar{4}-4+\bar{1}|$$

$$|-3\rangle \equiv |\varepsilon\theta\zeta+1-1+4+\bar{1}-4-\bar{4}|$$

$$\begin{aligned}|+9a\rangle \equiv [&5\{|\varepsilon\theta\zeta+1-1+4+\bar{4}-4+\bar{5}|\\ &+|\varepsilon\theta\zeta+1-1+4+\bar{4}-\bar{4}+5|\}\\ &-2\{|\varepsilon\theta\zeta+1-\bar{1}+4+\bar{4}-4+5|\\ &+|\varepsilon\theta\zeta+\bar{1}-1+4+\bar{4}-4+5|\\ &+|\varepsilon\bar{\theta}\zeta+1-1+4+\bar{4}-4+5|\\ &+|\varepsilon\bar{\theta}\zeta+1-1+4+\bar{4}-4+5|\\ &+|\bar{\varepsilon}\theta\zeta+1-1+4+\bar{4}-4+5|\}]/\sqrt{70}\end{aligned}$$

$$\begin{aligned}|+1a\rangle \equiv [&5\{|\varepsilon\theta\zeta+1-1+4+\bar{5}-4-\bar{4}|\\ &+|\varepsilon\theta\zeta+1-1+\bar{4}+5-4-\bar{4}|\}\\ &-2\{|\varepsilon\theta\zeta+1-\bar{1}+4+5-4-\bar{4}|\\ &+|\varepsilon\theta\zeta+\bar{1}-1+4+5-4-\bar{4}|\\ &+|\varepsilon\bar{\theta}\zeta+1-1+4+5-4-\bar{4}|\\ &+|\varepsilon\bar{\theta}\zeta+1-1+4+5-4-\bar{4}|\\ &+|\bar{\varepsilon}\theta\zeta+1-1+4+5-4-\bar{4}|\}]/\sqrt{70}\end{aligned}$$

$$\begin{aligned}|+9b\rangle \equiv \{&|\varepsilon\theta\zeta+1-1+4+\bar{4}-4+\bar{5}|\\ &-|\varepsilon\theta\zeta+1-1+4+\bar{4}-\bar{4}+5|\}/\sqrt{2}\end{aligned}$$

$$\begin{aligned}|+1b\rangle \equiv \{&|\varepsilon\theta\zeta+1-1+4+\bar{5}-4-\bar{4}|\\ &-|\varepsilon\theta\zeta+1-1+\bar{4}+5-4-\bar{4}|\}/\sqrt{2},\end{aligned}$$

where no bar implies spin α, a bar implies spin β and the molecular orbitals are denoted by their λ_z values.

The energies of the excited sextets including porphin triplets (^6E_T, $|\pm 9a\rangle$ and ^6E_T, $|\pm 1a\rangle$), porphin Q and B singlets (^6E_Q, $|\pm 9b\rangle$ and ^6E_B, $|\pm 1b\rangle$), and "porphin to high-spin iron(III)" charge-transfer states ($^6E_{CT}$, $|\pm 5\rangle$ and $^6E_{CT}$, $|\mp 3\rangle$) are given in Table 3 in terms of energy parameters E, E_{CT}, K_1, and K_9, where $K_1 \equiv K+K''$ and $K_9 \equiv K-K''$. The mixing terms are also given in Table 3 in terms of delocalization parameter β and off-diagonal corrections for the circular box model. As stated before, we have $\varepsilon \equiv E'+2K'$ and $\varepsilon' \equiv E'$. An off-diagonal term between the charge-transfer states

$$\varepsilon'' \equiv \{\varepsilon(1a_1)-\varepsilon(3a_2)\}/2+\{(a_1a_1|d\pi d\pi)-(a_2a_2|d\pi d\pi)\}/2$$

is introduced. Coulomb repulsions $(a_1a_1|d\pi d\pi)$ and $(a_2a_2|d\pi d\pi)$, however, are less sensitive to the angular nodal character of the wave functions involved and do not differ much from other. Thus ε'' should be rather small.

To reproduce the transition energies and the intensity ratio of Q and B bands of TPPCo(II), it has been assumed that

$$E = 14810\ \text{cm}^{-1},\ K_1 = 4600\ \text{cm}^{-1},\ K_9 = 2530\ \text{cm}^{-1}$$

and $\varepsilon = \varepsilon' = \pm 1480\ \text{cm}^{-1}$.[24] Since a change in E was expected for tervalent central metal ion, the parameters were readjusted to give a better description of the spectrum of TPPCo(III)Cl complex:

$$E = 13070\ \text{cm}^{-1},\ K_1 = 4600\ \text{cm}^{-1},\ K_9 = 2730\ \text{cm}^{-1}$$

and $\varepsilon = \varepsilon' = \pm 1340\ \text{cm}^{-1}$. From the coefficients on nitrogens of the molecular orbital 4e[17] and a value of resonance integral assumed by Hanazaki and Nagakura for a calculation of tris(bipyridine)iron(II) complex,[25] β was obtained as $-3000\ \text{cm}^{-1}$. The lowest excited sextets were calculated for a variety of E_{CT} and ε's. They are shown as a function of E_{CT} in Fig. 9. The lowest excitations of high-spin TPPFe(III)X complex (Fig. 10) are well reproduced $E_{CT} = 12500\ \text{cm}^{-1}$. Contributions of the composite excited states to each of the lowest excited states are given in Table 4, together with the effective numbers of the transferred charge in the excited states. The MCD spectrum of TPPFe(III)-Cl in benzene (Fig. 3) shows a normal A-term dispersion in each absorption band. This reveals that each of the lowest excited states is degenerate and has a characteristic orbital angular momentum. The value

24) H. Kobayashi, T. Hara, and Y. Kaizu, This Bulletin, **45**, 2148 (1972).

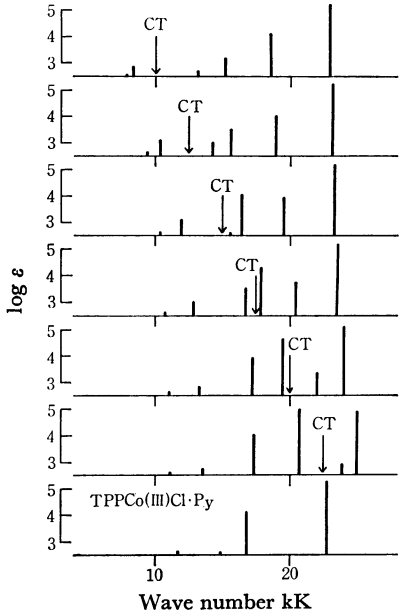

Fig. 9. The lowest excited sextets of TPPFe(III)X calculated as a function of E_{CT}. CT implies the assumed E_{CT}.

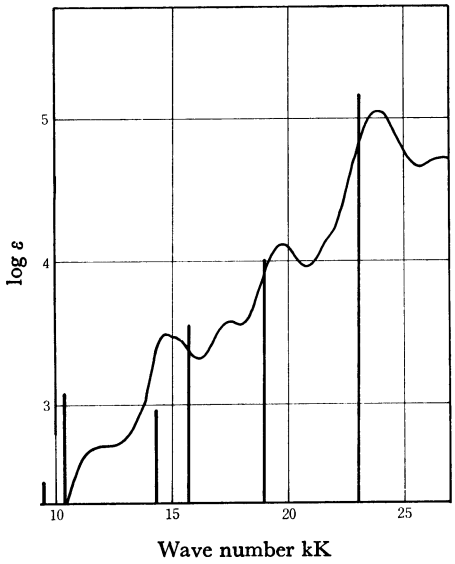

Fig. 10. The calculated lowest excitations of TPPFe(III)X. The assumed parameter values are $E=13070\ cm^{-1}$, $E_{CT}=12500\ cm^{-1}$, $K_1=4600\ cm^{-1}$, $K_9=2730\ cm^{-1}$, $\beta=-3000\ cm^{-1}$, $\varepsilon=1340\ cm^{-1}$, $\varepsilon'=-1340\ cm^{-1}$, and $\varepsilon''=0\ cm^{-1}$.

Table 4. Calculated compositions of the excited sextet states of high-spin iron(III) porphin

	a^{6}E	b^{6}E	c^{6}E	d^{6}E	e^{6}E	f^{6}E
Excitation energy (cm^{-1})	9410	10400	14300	15700	19000	23100
log ε	2.43	3.08	2.97	3.55	4.01	5.16
$^6E_{CT}$ ($\Lambda_z=\pm5$)	0.5017	−0.5681	−0.4875	0.2481	−0.3502	−0.0616
$^6E_{CT}$ ($\Lambda_z=\mp3$)	0.4505	0.6024	−0.4921	−0.3713	0.1246	−0.1967
^6E_T ($\Lambda_z=\pm9$)	0.5274	−0.3336	0.5286	−0.5497	0.1699	0.0090
^6E_T ($\Lambda_z=\pm1$)	0.5017	0.3981	0.4313	0.6270	−0.0916	0.0478
^6E_T ($\Lambda_z=\pm9$)	0.1074	−0.1690	−0.2139	0.2725	0.8665	0.2983
^6E_S ($\Lambda_z=\pm1$)	0.0631	0.1267	−0.0949	−0.1763	−0.2715	0.9307
Λ_z ($\hbar$)	±3.51	±1.96	±3.58	±3.71	±7.67	±1.57
Number of the transferred charge	0.455	0.686	0.480	0.199	0.138	0.042

The assumed parameter values are $E=13070\ cm^{-1}$, $E_{CT}=12500\ cm^{-1}$, $K_1=4600\ cm^{-1}$, $K_9=2730\ cm^{-1}$, $\beta=-3000\ cm^{-1}$, $\varepsilon=1340\ cm^{-1}$, $\varepsilon'=-1340\ cm^{-1}$, and $\varepsilon''=0\ cm^{-1}$.

of the orbital angular momentum in porphin excited state calculated by the circular box model (Table 4) is just an index of the orbital angular momentum but can predict a correct sign of A-term dispersion.[24] However, the molecular orbital calculations in a rather sophisticated form have given a wrong sign of A-term dispersion in the B band.[26]

Contributions of the "porphin to metal" charge-transfer excited states depend upon dπ electron affinity of the π electron-accepting metal ion. The electron affinity is estimated by application of the method of Griffith[27] using atomic spectroscopic data.[28] Differences between the dπ electron affinities of high-spin manganese(III), high-spin iron(III) and low-spin iron(III) are evaluated as shown in Table 5. The order of the electron affinity is low-spin Fe(III)>high-spin Fe(III)>high-spin Mn(III). Since σ-donation of the porphin nitrogens neutralizes the positive charge of the central metal ion, the electron affinity should be corrected for the electroneutralization effect.[29] The correction must be sizable, however, the ordering obtained above is still applicable to the metal ion in complex. A higher tendency of reduction is expected for a molecular environment to stabilize the low-spin iron(III) porphin, but the "porphin to iron" charge-

25) I. Hanazaki and S. Nagakura, *Inorg. Chem.*, **8**, 648 (1969).
26) A. J. McHugh, M. Gouterman, and C. Weiss, Jr., *Theoret. Chim. Acta*, **24**, 346 (1972).
27) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press (1961), p. 100.
28) C. E. Moore, "Atomic Energy Levels," Vol. 2, National Bureau of Standards, Washington (1952).
29) I. Fujita, T. Yazaki, Y. Torii, and H. Kobayashi, This Bulletin, **45**, 2156 (1972).

TABLE 5. $d\pi$ ELECTRON AFFINITY

Species	Configuration energy		Electron affinity (E_a)	ΔE_a
Mn(III)	Mn(III) d^4	$-4U+6A-21B$	$-\phi'+2B+6C$ constant-29.31 eV	
high-spin	Mn(II) d^5	$-5U+10A-19B+6C$		
				1.33 eV
Fe(III)	Fe(III) d^5	$-5U+10A-35B$	$-\phi+7C$ constant-30.64 eV	
high-spin	Fe(II) d^6	$-6U+15A-35B+7C$		
				2.27_5 eV
Fe(III)	Fe(III) d^5	$-5U+10A-20B+10C$	$-\phi-10B+5C$ constant-32.91_5 eV	
low-spin	Fe(II) d^6	$-6U+15A-30B+15C$		

Electron attaching process

Mn(III) high-spin: Mn(III) [d^4: $(xy)(yz)(zx)(z^2)$]+e → Mn(II)[d^5: $(xy)(yz)^2(zx)(z^2)$]

Fe(III) high-spin: Fe(III)[d^5: $(xy)(yz)(zx)(z^2)(x^2-y^2)$]+e → Fe(II)[$d^6$: $(xy)(yz)^2(zx)(z^2)(x^2-y^2)$]

Fe(III) low-spin: Fe(III)[d^5: $(xy)^2(yz)(zx)^2$]+e → Fe(II)[d^6: $(xy)^2(yz)^2(zx)^2$]

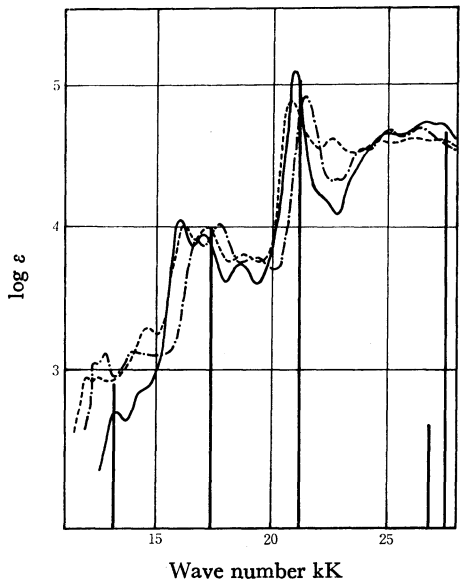

Fig. 11. Absorption spectra of TPPMn(III)Cl·H_2O.
——: benzene solution – – –: pyridine solution
–·–·–: methanol solution
Vertical lines imply calculated spectra.

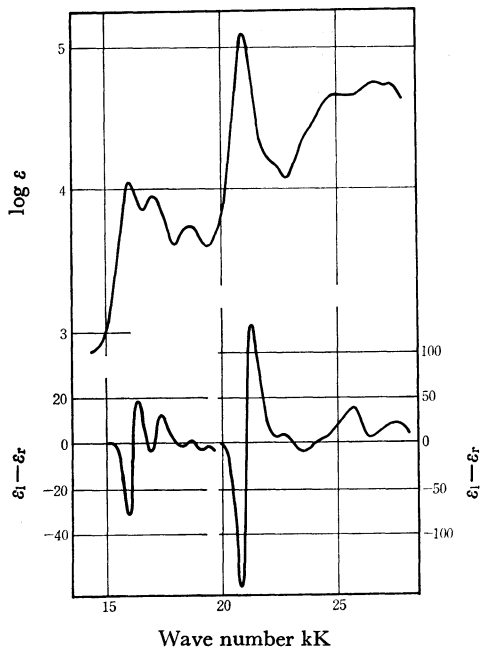

Fig. 12. MCD spectrum of TPPMn(III)Cl·H_2O in benzene.
Upper: absorption spectrum Lower: MCD spectrum

transfer excited states are too low to cause an appreciable interaction with the porphin (π, π^*) excited states. In fact, a spectrum assigned to the low-spin iron(III) porphyrin by George *et al.*[14] does not differ much from the (π, π^*) spectrum of typical metal porphyrin.

The charge-transfer states in high-spin manganese(III) porphin must be as high as the porphin B state. In fact, a remarkable splitting of the B band is observed (Fig. 11). The charge-transfer excited states slightly higher than B state push down the B state and grant an intensity to the porphin singlet-triplet excitations by similar configuration interactions as in the case of high-spin iron(III) porphin. The energy matrices are given in Table 3. The absorption spectrum of TPPMn(III)Cl·H_2O was well reproduced (Fig. 11) by a calculation assuming $E_{CT}=25000$ cm^{-1}, $\beta=-4000$ cm^{-1}. The MCD spectrum of TPPMn(III)Cl·H_2O in benzene is shown in Fig. 12. A normal A-term MCD dispersion with $A/D=1$ was observed in the 21000 cm^{-1} band. Boucher also obtained a similar MCD spectrum of protoporphin IX dimethylester manganese(III) chloride in chloroform.[9] Such spectrum has been observed in the B band of typical metal porphins. Mixing of the "porphin to manganese(III)" charge-transfer excitations gives rise to a remarkable spectral shift and a redistribution of spectral intensity, but the 21000 cm^{-1} transition is still predominantly made of B excitation (Table 6). The value of β in high-spin manganese(III) was assumed to be slightly higher than that of high-spin iron(III) so as to reproduce the observation. The iron(III) in TPPFe(III)Cl is pentacoordinate and is out-of-plane from the coordinating nitrogens according to X-ray studies, whereas the manganese(III) in TPPMn(III)Cl·H_2O is

TABLE 6. CALCLUATED COMPOSITIONS OF THE EXCITED QUINTET STATES OF HIGH-SPIN MANGANESE(III) PORPHIN

	a^5E	b^5E	c^5E	d^5E	e^5E	f^5E
Excitation energy (cm^{-1})	10800	13200	17400	21200	26800	27500
log	2.00	2.89	3.98	5.02	2.61	4.66
${}^5E_{CT}$ ($\Lambda_z=\pm5$)	0.1797	0.2265	0.2327	0.1547	0.8961	0.1882
${}^5E_{CT}$ ($\Lambda_z=\pm3$)	0.1734	−0.2188	−0.0523	0.4417	−0.2151	0.8228
${}^5E_T$ ($\Lambda_z=\pm9$)	0.6860	0.6514	−0.2212	−0.0358	−0.2329	−0.0271
${}^5E_T$ ($\Lambda_z=\pm1$)	0.6799	−0.6691	0.1107	−0.1835	0.0768	−0.1954
${}^5E_S$ ($\Lambda_z=\pm9$)	0.0598	0.1439	0.8975	0.2536	−0.2976	−0.1316
${}^5E_S$ ($\Lambda_z=\pm1$)	0.0359	−0.0899	−0.2764	0.8251	0.0459	−0.4810
Λ_z ($\hbar$)	±4.80	±4.57	±8.04	±0.68	±5.18	∓1.42
Number of the transferred charge	0.062	0.099	0.057	0.220	0.849	0.713

The assumed parameter values are $E=13070\ cm^{-1}$, $E=25000\ cm^{-1}$, $K_1=4600\ cm^{-1}$, $K_0=2730\ cm^{-1}$, $\beta=-4000\ cm^{-1}$, $\varepsilon=1340\ cm^{-1}$, $\varepsilon'=-1340\ cm^{-1}$, and $\varepsilon''=0\ cm^{-1}$.

hexacoordinate and must be in the nitrogen plane. Thus the conjugation between the central ion and porphin is increased in TPPMn(III)Cl·H_2O.

Since metal dπ and the lowest vacant π orbitals 4e are of the same symmetry, an electron delocalization between them occurs appreciably when they are energetically close to each other. The delocalization effect grants the charge-transfer excitation an intensity of the allowed B excitation, although the pure charge-transfer excitation, in principle, is forbidden. In the case of open-shell configurations such as in high-spin iron(III) and high-spin manganese(III), the charge-transfer state causes a connection not only with singlet but also with triplet (π, π^*) states, making the singlet-triplet (π, π^*) excitations partially allowed. Thus the complex spectra of high-spin iron(III)- and manganese(III) porphyrins are assigned to the excited states arising from the configuration interactions of porphyrin excited triplet and singlet (π, π^*) states and "porphyrin to metal" charge-transfer excited states.

Our sincere thanks are due to Dr. Kiyoko Yamamoto for her advice concerning the preparation of tetraphenylporphin, and also to Dr. Kazuo Shibata for his suggestion on the opal glass method. One of the authors (H. K.) wishes to thank Profs. M. Kotani, W. S. Caughey, and M. P. Gouterman for their helpful discussions.