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Electronic Spectra and Electronic Structure of Iron(II) Tetraphenylporphins

Hiroshi KOBAYASHI and Yasuo YANAGAWA

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

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Tetraphenylporphiniron(II) was synthesized and isolated in a pure state. The iron(II) porphin was in the state of $S=2$. The spin state of iron(II) porphin varies with the axial ligand field. Oxygeneous axial ligands such as tetrahydrofuran and dioxane gave an intermediate spin state ($S=1$), while nitrogeneous ligands such as pyridine gave a diamagnetic state ($S=0$). The electronic spectra of tetraphenylporphin complexes of iron(II) were measured for the three types of the spin state.

Iron of the prosthetic groups in hemoglobin and myoglobin participates as a ferrous ion in oxygen carrying. Iron(II) is stable against oxidation in the hemoproteins even though it is directly bound with an oxygen molecule, whereas iron(II) in the synthetic complexes is hardly stable in the presence of oxygen. Iron(II) in the synthetic porphyrins is not so stable in the presence of oxygen and moisture in the air. However, iron(II) is fairly stabilized in the diamagnetic state obtained for a strong ligand field such as in tris(2,2′-bipyridine)-, tris(1,10-phenanthroline)- or hexacyano complex. The iron(II) porphyrin with a strong axial field is in a diamagnetic state and is relatively stabilized against oxidation.

A systematic study of the effect of axial ligands to the electronic structure of the iron(II) porphyrins was found necessary for the synthetic porphyrins. Recently we succeeded in the preparation of a new series of iron(II) complexes of tetraphenylporphin. In this paper, we present their electronic absorption spectra with special attention to the spin state of the central iron(II).

Experimental

Synthesis of Tetraphenylporphinbis(pyridine)iron(II). Tetraphenylporphinbis(pyridine)iron(II), TPPFe(II)·2Py (TPP is an abbreviation of tetraphenylporphin and Py, pyridine) was prepared by two different methods in a vacuum system.

(A) *Reduction of TPPFe(III)X Complex.* Tetraphenylporphiniron(III) acetate, TPPFe(III)OCOCH$_3$, (500 mg) was dissolved in a mixed solvent of 20 m*l* of pyridine, 150 m*l* of chloroform and 80 m*l* of methanol. After bubbling with dried nitrogen, 300 mg of sodium borohydride was added to the solution. The mixture was stirred for 3 hr at 50—60°C. Chloroform and methanol were distilled off until the volume of the solution became 20—30 m*l*. About 100 m*l* of methanol saturated with dried nitrogen, was added to the concentrated solution. After the solution had been allowed to stand for several hours, blue violet crystals were collected, washed several times with methanol saturated with dried nitrogen and dried in a vacuum. Since TPPFe(II)·2Py was sensitive to the air, it was kept in a glass capsule with inert gas.

(*B*) *Reaction of Iron(II) Acetate with the Metal-Free Base of TPP.* The metal-free base (500 mg) was dissolved in a mixed solvent of 20 m*l* of pyridine and 50 m*l* of chloroform. The solution was sufficiently saturated with dried nitrogen and to it was quickly added about 130 m*l* of a saturated solution of iron(II) acetate in acetic acid prepared by refluxing iron powder in acetic acid saturated with dried nitrogen. Care was taken not to contaminate the porphin solution by unreacted iron powder. The mixture was stirred for 3 hr at 50—60°C. Blue violet crystals were collected and kept in the same way as in (A).

The products prepared by both methods were identified by their characteristic absorption spectra. The product prepared by the method (A) was also identified by elemental analysis.

Found: C, 77.57; H, 4.81; N, 9.99; Fe, 6.80%. Calcd for $C_{54}H_{38}N_6Fe$: C, 78.47; H, 4.88; N. 10.17; Fe, 6.76%.

Synthesis of Tetraphenylporphiniron(II). A capsule of TPPFe(II)·2Py was joined to a vacuum line of 10^{-2} mmHg and was heated for 5 hr in an oil bath at 200°C. TPPFe(II) was obtained in reddish purple crystalline state. It was much more sensitive to the air than TPPFe(II)·2Py, and was kept in a glass capsule in a vacuum.

Found: C, 80.89; H, 4.35; N, 8.53; Fe, 8.30%. Calcd for $C_{44}H_{28}N_4Fe$: C, 79.00; H, 4.52; N, 8.41; Fe, 8.34%.

Synthesis of Tetraphenylporphinbis(tetrahydrofuran)iron(II). TPPFe(II)·2THF (THF is an abbreviation of tetrahydrofuran) could not be synthesized by the same method as for TPPFe(II)·2Py. This was because of unstable binding of iron(II) and tetrahydrofuran. TPPFe(II)·2THF was prepared from TPPFe(II) with the apparatus shown in Fig. 1. The apparatus was joined to a vacuum line. From C, TPPFe(II)·2Py was carefully placed at the bottom of A under dried nitrogen atmosphere. TPPFe(II)·2py was heated for 5 hr in an oil bath at 200°C, while the apparatus was being evacuated by a vacuum line. After the reaction product had been allowed to stand at room temperature, a sufficient amount of THF saturated with dried nitrogen was added to the reaction product at A. While the THF solution in branch A was cooled in liquid nitrogen, the apparatus was sealed at X and evacuated by a vacuum line. After the cock D had been closed, the frozen solution was allowed to stand at room temperature. The solution was shaken for a while. The solvent THF was then completely transferred to branch B by cooling the branch in liquid nitrogen. Cooling of the frozen THF in the branch B was continued in liquid nitrogen. The apparatus was evacuated down to 10^{-2} mmHg, while the reaction product at A was allowed to stand at room temperature to dry. When the product was dried, the apparatus was sealed off at Y and the product was transferred into a branch of capsules. The branch of capsules was then sealed off at Z.

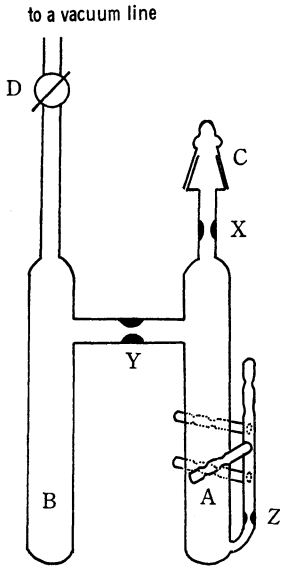

Fig. 1. Apparatus for preparation of TPPFe(II).

Found: C, 74.95; H, 4.79; N, 7.06; Fe, 6.91%. Calcd for $C_{52}H_{44}N_4O_2Fe$: C, 76.82; H, 5.45;N, 6.92; Fe, 6.87%.

Synthesis of Tetraphenylporphinbis(pyridine)manganese(II). Tetraphenylporphinmanganese(III) chloride, TPPMn(III)Cl, (500 mg) was dissolved in a mixed solvent of 20 m*l* of pyridine, 40 m*l* of chloroform and 140 m*l* of methanol. After bubbling with dried nitrogen, 300 mg of sodium borohydride was added to the solution. The mixture was vigorously stirred for 3 hr at 50—60°C. After the reaction mixture was concentrated to 10—30 m*l* by distillation, the crystal of tetraphenylporphinbis(pyridine)manganese(II), TPPMn(II)·2Py, was precipitated by addition of methanol saturated with dried nitrogen. Blue violet lustrous crystals were collected, washed several times with dried oxygen-free methanol, and kept in a glass capsule with dried nitrogen. Since TPPMn(II)·2Py was sensitive to oxygen and moisture in the air, the whole process should be carried out under nitrogen atmosphere.

Found: C, 78.74; H, 4.36; Mn, 6.63%. Calcd for $C_{54}H_{38}N_6Mn$: C, 78.53; H, 4.46; Mn, 6.65%. Manganese was oxidized to permanganate and was determined by colorimetry.

Measurements of Absorption Spectra. Electronic absorption spectra were measured by a Shimadzu automatic recording spectrophotometer Model MPS-50 and a Beckman DU spectrophotometer using quartz cells of 0.1 cm or 1 cm light path. The solvents for absorption measurement were benzene, pyridine, piperidine, tetrahydrofuran, and dioxane purified by the usual methods.[1] They were distilled just before the use and degassed by successive freeze-thaw pumping cycles. Solutions for measurements were prepared in a vacuum system.

Measurements of Magnetic Susceptibilities. Magnetic moments were determined by means of the Gouy method.[2] Measurements were carried out at room temperature with the sample sealed in a capsule with dried nitrogen. After calibrating for the diamagnetic term, the magnetic moment of complex was calculated from the data obtained.

Results and Discussion

Tetraphenylporphiniron(II) has a planar structure as shown in Fig. 2. The central iron might be slightly out of the porphin plane. Such a structure has been found in various metal porphyrins including metal tetraphenylporphins.[3,4] Iron(II) in tetraphenylporphiniron(II), a planar complex, is in the spin state of $S=2$. In the case of TPPFe(II)·2Py, however, σ donation of the nitrogeneous donor of two coordinating pyridines gives rise to a strong axial field and all spins in the central iron are quenched ($S=0$). This was shown by magnetic susceptibility measure-

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

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

[3] J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Amer. Chem. Soc.*, **85**, 2334 (1963); E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, **86**, 2342 (1964).

[4] 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; M. F. Perutz, *Scientific American*, **211**, 5 (1964); J. C. Kendrew, *Science*, **139**, 1259 (1963).

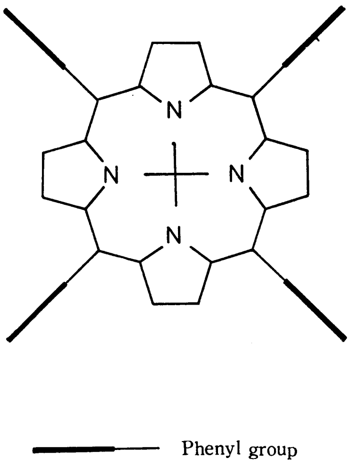

Fig. 2. Molecular geometry of metal tetraphenylporphin. Phenyl groups are actually perpendicular to the molecular plane of porphin.

ments. When the axial ligand field is of moderate strength, the central iron might be in the intermediate spin state, $S=1$. The ligand field of intermediate strength is furnished by such a relatively weak ligand as oxygeneous donor of tetrahydrofuran or dioxane. TPPFe(II)·2THF showed an intermediate value of the magnetic moments for $S=0$ and $S=2$. If a thermal equilibrium exists between the states $S=0$ and $S=2$ of a complex, an intermediate value is expected to be the average of the magnetic moments of two components. In the case of Fe(III) porphyrins, a thermal equilibrium actually exists between two spin states of a complex, giving a mixture absorption spectrum of the species with different spin states.[5] TPPFe(II)·2THF, however, shows no mixture spectrum of the species $S=0$ and $S=2$, but a spectrum characteristic of a species in a spin state other than $S=0$ or $S=2$. Mössbauer spectrum also shows a spectrum characteristic of the intermediate spin state, which differs from a spectrum expected for a mixture of the high spin state and the diamagnetic one.[6] The observed magnetic moments are summarized in Table 1.

TABLE 1. MAGNETIC MOMENTS OF IRON(II)- AND MANGANESE(II) TETRAPHENYLPORPHINS

Complex	Magnetic moment (Bohr magneton)	Number of unpaired electrons	Spin state
TPPFe(II)·2Py	0	0	$S=0$
TPPFe(II)·2THF	2.75	2	$S=1$
TPPFe(II)	4.75	4	$S=2$
TPPMn(II)·2Py	6.02	5	$S=5/2$

TPP: Tetraphenylporphin, Py: Pyridine, and THF: Tetrahydrofuran.

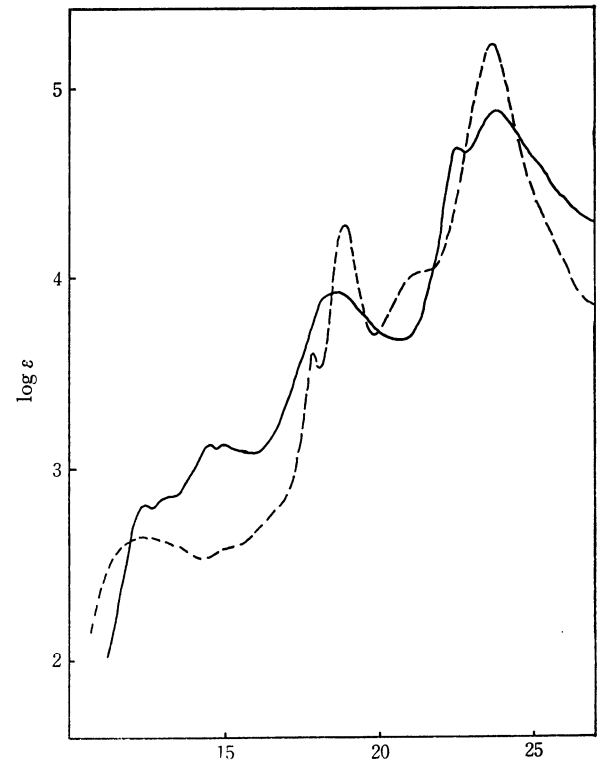

Fig. 3. Absorption spectrum of TPPFe(II).
——: benzene solution
----: pyridine solution

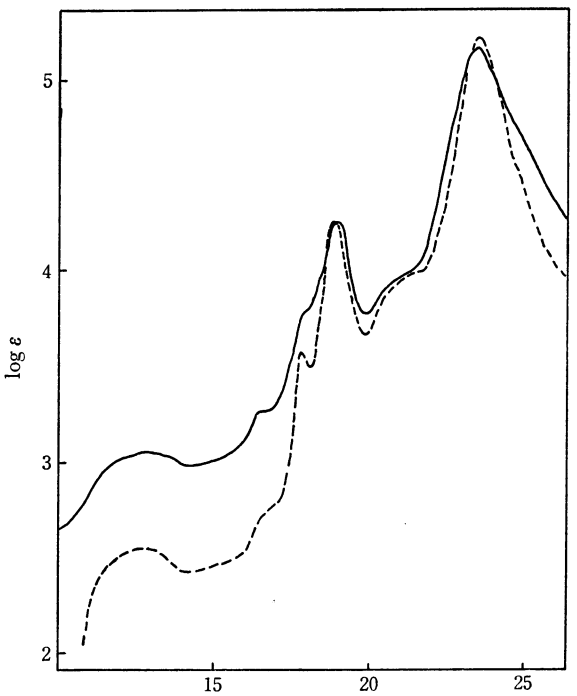

Fig. 4. Absorption spectrum of TPPFe(II)·2Py.
——: benzene solution
----: pyridine solution

The absorption spectra of TPPFe(II) and TPPFe(II)·2Py were measured in benzene and in pyridine (Figs. 3 and 4). Since the absorption spectrum of TPPFe(II) in pyridine solution was in good agreement with that of TPPFe(II)·2Py in pyridine solution, two

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

[6] H. Kobayashi, Y. Maeda, and Y. Yanagawa, This Bulletin, **43**, 2342 (1970).

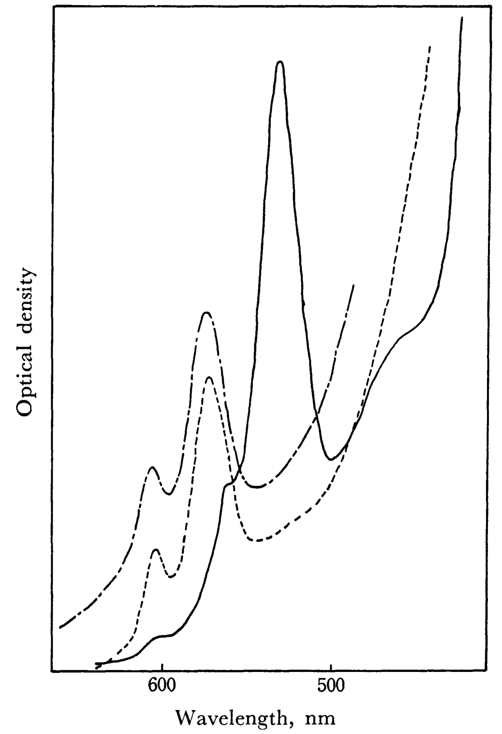

Fig. 5. Spectral change of TPPFe(II)·2Py in benzene when exposed to the air.
——: TPPFe(II)·2Py in dried oxygen-free benzene
----: after the benzene solution was exposed to the air
-·-·: $(TPPFe(III))_2O\cdot 2H_2O$ in benzene

molecules of pyridine coordinate to the iron(II) in TPPFe(II) upon dissolution in pyridine. The spectra in the visible region of TPPFe(II)·2Py both in benzene and in pyridine actually coincide. The absorption spectrum of the powder sample of TPPFe(II)·2Py measured by means of the opal glass technique[7] was in good agreement with the solution spectrum. This indicates that the coordination of pyridine in the molecular crystal does not differ much from that in solution. Among the iron(II) complexes of tetraphenylporphin, bis(pyridine) complex in the solid state seems to be the most inert to oxygen and moisture in the air. However, it is readily converted into a ferric complex such as $(TPPFe(III))_2O\cdot 2H_2O$,[8] when the benzene solution of TPPFe(II)·2Py is exposed to the air (Fig. 5).

The absorption spectrum of TPPFe(II) in THF differs from those observed in benzene ($S=2$) and in pyridine ($S=0$). The visible bands observed in THF are close to those observed in benzene, while the Soret band in THF is in fairly good agreement with that in pyridine. The spectrum of TPPFe(II) in THF can not be reproduced by a superposition of the spectra of high spin component and diamagnetic one. Since the intensity of the characteristic bands is almost in the same order in these two components, the mixture spectrum should be a simple superposed spectrum. The observed spectrum of TPPFe(II) in THF is not a simple superposed mixture spectrum. Thus it should be assigned to a spectrum characteristic of a single species other than high spin species or diamagnetic species. As a matter of fact, we could isolate solid TPPFe(II)·2THF from the THF solution of TPPFe(II). It shows an intermediate spin value. TPPFe(II) in dioxane shows a very similar spectrum to that in THF (Fig. 6).

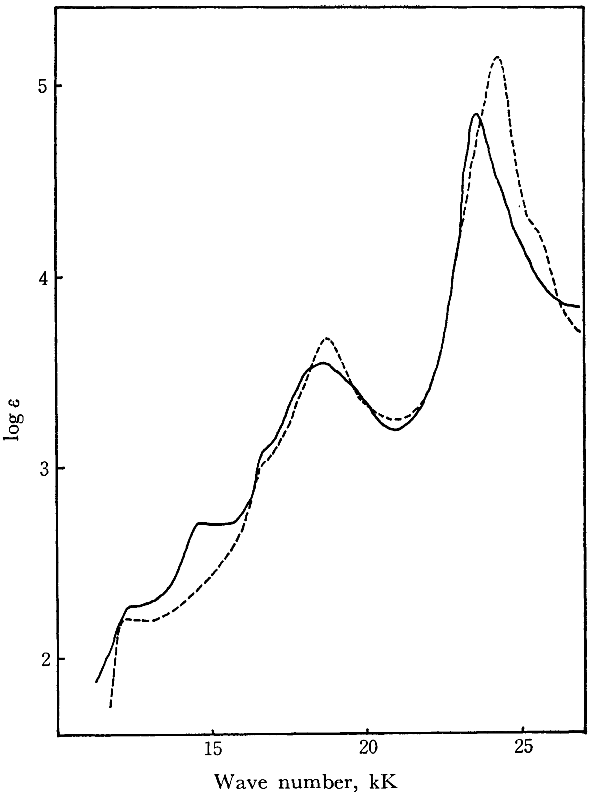

Fig. 6. Absorption spectra of TPPFe(II) in tetrahydrofuran and dioxane.
——: THF solution
----: dioxane solution

In the case of Fe(III) complexes of tetraphenylporphin, high spin species ($S=5/2$) and low spin species ($S=1/2$) have been synthesized, but not the intermediate spin species ($S=3/2$).[6] In the case of Fe(II) complexes, however, three spin states could be obtained. The most probable *d* electron configurations of these three spin states are given in Fig. 7. The ordering of the ligand-fielded *d* orbitals is schematically shown in Fig. 8. The actual values obtained

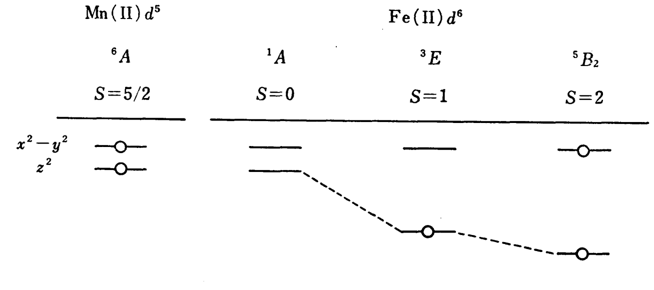

Fig. 7. Configuration of *d* electrons in iron(II)- and manganese(II) tetraphenylporphins.

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

[8] I. A. Cohen, *J. Amer. Chem. Soc.*, **91**, 1980 (1969); E. B. Fleischer and T. S. Srivastava, *J. Amer. Chem. Soc.*, **91**, 2403 (1969).

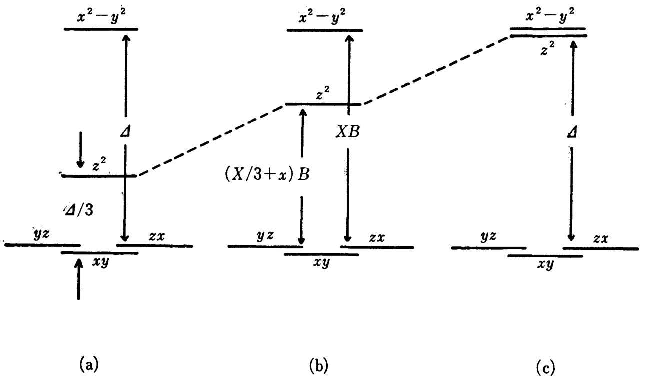

Fig. 8. Energy levels of the ligand-fielded *d* orbitals.
(a) planar configuration
(b) planar configuration+axial ligand field
(c) octahedral configuration

depend on the model employed. However, a simple argument in terms of molecular orbital theory can readily give the ordering of split *d* orbitals.[9] The ordering in a planar ligand field:

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

Δ is the ligand-field splitting parameter. For the sake of simplicity, the small energy difference between yz, zx, and xy orbitals is ignored. Energy difference between x^2-y^2 and z^2 orbitals is crucial. It varies with the axial ligand field. $\varepsilon(x^2-y^2)-\varepsilon(z^2)$ is $2\Delta/3$ for a planar configuration, while it vanishes for an octahedral configuration. $\varepsilon(z^2)$ is parametrized as $\Delta/3+xB$, where xB is an index of the axial ligand field strength in terms of Racah's parameter B. The energy values of d orbitals in iron porphin, in general, are given in B units as follows: $\varepsilon(x^2-y^2)=\Delta=XB$, $\varepsilon(z^2)=\Delta/3+xB=(X/3+x)B$, $\varepsilon(xy)=\varepsilon(yz)=\varepsilon(zx)=0$. The energy of the ground state of iron(II) porphin can be approximately given as a function of the ligand field strength XB, the axial ligand field strength xB and Racah's electrostatic interaction parameters B and C.

$$^1A_1 \qquad E_0-30B+15C$$

$$^3E \qquad E_0-26B+12C+\frac{2}{3}XB+\frac{1}{2}xB$$
$$-\frac{B}{2}\sqrt{\frac{4}{9}X^2+\frac{16}{3}X-\frac{4}{3}xX+x^2-8x+64}$$

$$^5B_2 \qquad E_0-35B+7C+\frac{4}{3}XB+xB$$

where E_0 denotes a common term of spherical symmetry. Assuming an empirical relationship $C=4B$,[10] we have

$$^1A_1-{}^5B_2 \quad \left(37-\frac{4}{3}X-x\right)B$$

$$^3E-{}^5B_2 \quad \left(29-\frac{2}{3}X-\frac{1}{2}x\right.$$
$$\left.-\frac{1}{2}\sqrt{\frac{4}{9}X^2+\frac{16}{3}X-\frac{4}{3}xX+x^2-8x+64}\right)B$$

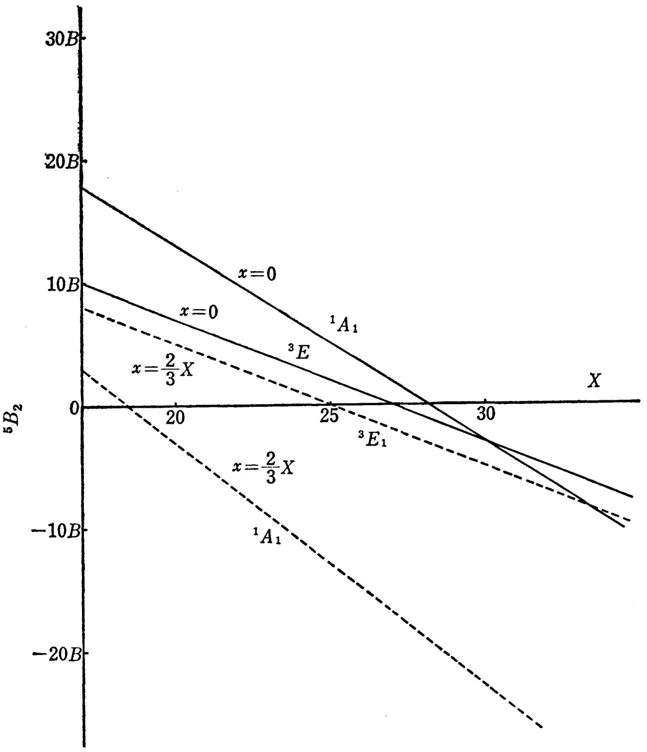

Fig. 9. Energy diagram as a function of the ligand field strength, X, and the axial ligand field strength, x.
----: $x=2/3X$ (octahedral configuration)
——: $x=0$ (planar configuration)

The energy diagram is readily drawn as a function of X and x and is shown in Fig. 9. $^1A_1$ and ^3E are stabilized to a greater extent than $^5B_2$ when X increases. With a fixed value of X, $^1A_1$ is more stabilized than ^3E when the axial ligand field x increases. Unless the axial field is fairly weak, the ground state could not be ^3E. B in iron(II) porphin is estimated to be about 800 cm^{-1} from spectroscopic data.[11] The value of Δ in porphin has been estimated to be 20,000—25,000 cm^{-1} by an extended Hückel molecular orbital calculation.[12] Thus X is in the region 25—31. The value of X predicts $^1A_1$ ground state for an octahedral environment, where $x=2/3X$ which is attained by strongly coordinating axial ligands. For an octahedral ligand field the intermediate spin state ^3E can not be the ground state. For a planar ligand field, where $x=0$, the ground state is $^5B_2$ if $X<27$ and ^1A if $X>30$. When $27<X<30$, the intermediate spin state ^3E is expected to be the ground state. As a matter of fact, the ground state of iron(II) phthalocyanine with no axial ligand is in the state of $S=1$.[13] The ground state of TPPFe(II), however, is in the state of $S=2$. The value of X in TPPFe(II) is smaller than that of iron(II) phthalocyanine. However, in the

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9) H. Yamatera, This Bulletin, **31**, 95 (1958).
10) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jap.*, **9**, 766 (1954).
11) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press (1961), p. 437.
12) M. Zerner, M. Gouterman, and H. Kobayashi, *Theoret. Chem. Acta*, **6**, 363 (1966).
13) B. W. Dale, R. J. P. Williams, C. E. Johnson, and T. L. Thorp, *J. Chem. Phys.*, **49**, 3441 (1968); B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *J. ibid.*, **49**, 3445 (1968); C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *ibid.*, **53**, 1643 (1970).

presence of relatively weak axial ligands such as THF and dioxane, the ground state becomes ^3E. The ^3E ground state, in principle, is reached with a similar X value as in TPPFe(II) as long as the axial ligand field is low. However, a mechanism to enhance the value of X is expected to get the ^3E ground state of TPPFe(II) in THF or dioxane. An effective radius of the central iron in the $^5B_2$ state is rather large and the iron can not be in the central hole and is slightly out of the porphin plane. Once ^3E state or ^1A state is attained, however, the effective radius of the iron is reduced and the iron can be seated in the central hole of porphin. Thus the overlap integral of iron and nitrogen orbitals and the X value increase. The effective radius depends on the occupation number in $d_{x^2-y^2}$ orbital which partially accepts σ electron donated by four nitrogens of porphin. The geometrical change has been pointed out by means of X-ray studies.[4]

TPPMn(II)·2Py in the solid state shows the highest spin state (Table 1). The powder spectrum of TPPMn(II) obtained by the opal glass method was very close to that in benzene. This indicates no change of spin state involved in dissolution. The solution spectrum of TPPMn(II)·2Py in benzene is shown in Fig. 10. The absorption bands are assigned to pure (π, π^*) transitions as that of TPPZn(II).[14] The lowest (π, π^*) transitions are described as a 50–50 admixture of transitions $2a_1 \rightarrow 4e$ and $3a_2 \rightarrow 4e$.[14–16] When the central metal ion has no appreciable π interaction with the conjugated system of porphin, the lowest excited states can be described by the four-orbital model.[14] When the four-orbital model is applicable, a gap between Q and B bands is fairly constant for a series of central metal ions. This can be seen in the spectra of TPPMn(II)·2Py and TPPZn(II) as shown in Fig. 10. If the central metal ion is replaced by a highly π-donating metal ion, the conjugated system of porphin in the ground and excited states should suffer π electron migration from the central metal ion. Although the absorption spectrum of diamagnetic TPPFe(II)·2Py apparently preserves a character of Q and B bands of a metal porphin less contributed by $d\pi$ electron, a gap between Q and B bands is remarkably smaller than those of TPPMn(II)·2Py and TPPZn(II). Since $d\pi$ ionization potential of the diamagnetic iron(II) in porphin is fairly low, the energy of the charge-transfer from metal $d\pi$ orbitals to the lowest antibonding ligand π orbitals is not so high. Both metal $d\pi$ orbitals zx and yz and the lowest antibonding porphin orbitals $4e$ are of E symmetry. Thus the "metal to ligand" charge-transfer states can mix with the ground state and the lowest exciting states of the π electron system of porphin. In the case of TPPFe(II)·2Py, weak absorption bands are observed in the near-infrared region. These weak bands might be assigned to "metal to porphin" and/or "metal to pyridine" charge-transfer transitions. However, the charge-transfer excited states and the Q and B excited states can not be very pure when their symmetries are the same and their energies are close. The lowest excited states representing the observed spectrum should be described in terms of a configuration interaction admixture of "metal to ligand" charge-transfer excited states and (π, π^*) excited state of porphin ring. As a result, lower charge-transfer states raise the Q state, and thus the gap of Q and B states are reduced. Another charge-transfer is possible from metal to axial ligand. When piperidine which lacks acceptable antibonding π molecular orbitals is used as the axial ligand, the possibility of the "metal to axial ligand" π charge-transfer can be eliminated. The spectrum of TPPFe(II) in piperidine still shows a contribution of charge-transfer states. The charge-transfer is ascribed to "iron to porphin." On the contrary, the spectrum of TPPFe(II) in pyridine gives an evidence of "iron to pyridine" charge-transfer transition at about 21 kK, whereas TPPFe(II) in piperidine lacks the absorption peak (Fig. 11).

Absorption spectrum of a coordination complex, in general, depends upon both the central metal and the ligands. In the case of metalloporphins, especially of iron porphins, the spectrum is predominantly influenced by the spin state of the central metal rather than particular axial ligands. The spin state of the central metal, however, depends upon the axial ligand

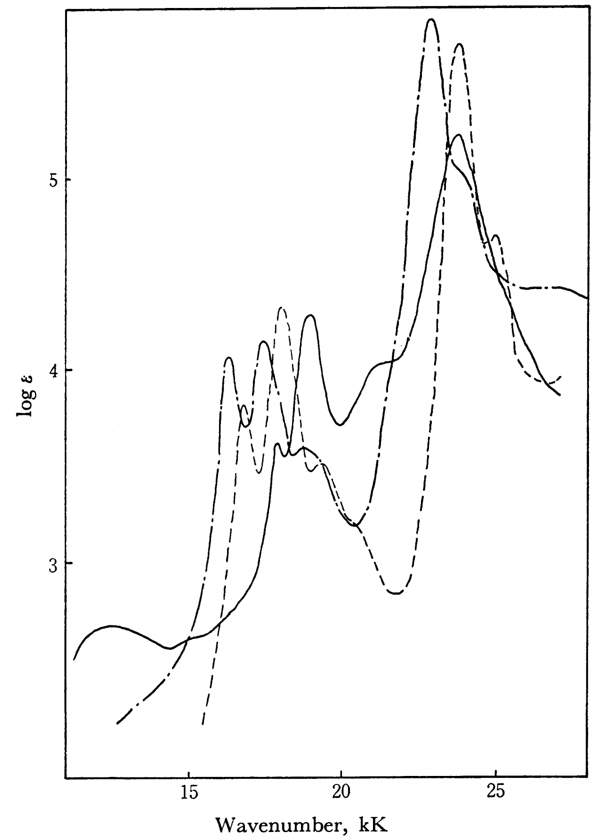

Fig. 10. Absorption spectrum of TPPMn(II)·2Py.
–·–·: TPPMn(II)·2Py in benzene
——: TPPFe(II)·2Py in pyridine
----: TPPZn(II) in THF

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[14] M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959).

[15] H. Kobayashi, *J. Chem. Phys.*, **30**, 1362 (1959).

[16] C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectrosc.*, **16**, 415 (1965).

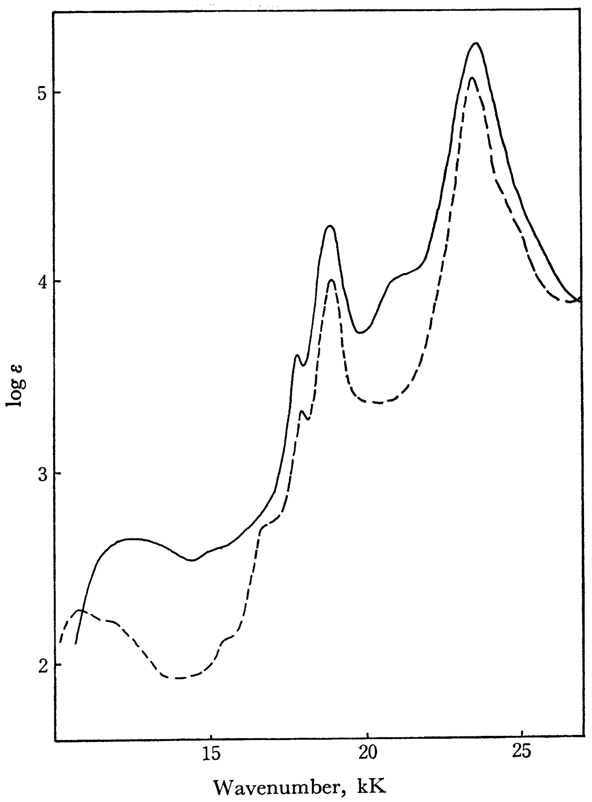

Fig. 11. Absorption spectra of TPPFe(II) in pyridine and piperidine.
——: pyridine solution
- - - -: piperidine solution

field and the spectrum varies with the axial ligands only when the axial ligands can change the spin state of the central metal. It should depend on the properties of the low energy absorption bands of metalloporphin.

When an open shell exists in the central metal ion as in TPPFe(II), "metal to ligand" or "ligand to metal" charge-transfer excited states can mix not only with singlet (π, π^*) excited states but also with triplet (π, π^*) excited states. When a delocalization interaction between iron $d\pi$ orbitals and $4e$ orbitals of porphin is sufficient, such a configuration mixing becomes significant. The usual metalloporphins have two pairs of the spin forbidden singlet-triplet transitions in the near-infrared region.[15,16] The lowest triplet emits phosphorescence. The charge-transfer interaction between the open shell iron and the excited states of porphin will carry an appreciable amount of transition probability to these spin forbidden transitions from the allowed transitions. As a matter of fact, TPPFe(II) shows a rather complicated spectrum in the lower energy region. The near-infrared bands of high spin porphin TPPFe(II), and also intermediate spin porphin TPPFe(II)·2THF should be assigned mainly to weak "metal to porphin" charge-transfer transitions. However, a contribution of the porphin triplets in the near-infrared absorption bands of the open shell iron(II) porphins should be pointed out. Generally speaking, the spin selection rule of molecular electronic transitions is released when the molecule is connected with an open shell system by a charge-transfer process.[17] If the interaction is not so strong as in TPPMn(II)·2Py, it shows just a weak absorption shoulder at the position of the lowest singlet-triplet transition. In the case of the open shell iron(II) porphins, however, the charge-delocalization effect increases mainly due to higher $d\pi$-donating power of iron(II) and thus a configuration mixing of various excitations gives rise to a shift in transition energy and also a redistribution of spectral intensity.

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[17] J. N. Murrell, *Mol. Phys.*, **3**, 319 (1960).