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Electronic Spectra of Tetraphenylporphinatoiron(III) Methoxide

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Tetraphenylporphinatoiron(III) methoxide in the high-spin state $S=5/2$ gives rise to an absorption spectrum which has been assigned to that of low-spin iron(III) porphyrins. The excited states characteristic of the spectrum of high-spin iron(III) porphyrins are the configuration-interaction admixtures of the lowest triplet and singlet porphyrin (π,π^*) excited states and the low-lying "porphyrin to iron(III)" charge-transfer excited states. The charge-transfer excited states in tetraphenylporphinatoiron(III) methoxide, however, are so high that the charge-transfer excited states are not sufficiently mixed with the lowest triplet (π,π^*) excited states. Thus the high-spin methoxo complex does not exhibit a spectrum characteristic of high-spin iron(III) porphyrins.

Possible spin states of the iron(III) ion embedded in porphyrin ligand are the high-spin state $S=5/2$ and the low-spin state $S=1/2$ depending upon its axial ligand field. The intermediate spin state $S=3/2$ is not obtained for a typical ligand field of porphyrin.[1-3] George, Beetlestone and Griffith separated the high- and low-spin spectral types for the ferrihemoproteins by combining spectroscopic and magnetic data.[4] They could get limiting spectra from the mixture spectra of the two spin states $S=5/2$ and $S=1/2$ in equilibrium. On the other hand, Caughey found that a high-spin iron(III) porphyrin, methoxo iron(III) deuteroporphyrin-IX dimethyl ester, shows an absorption spectrum characteristic of low-spin iron(III) porphyrins.[5,6]

In this paper, an interpretation of the low-spin type of spectrum observed for high-spin porphyrinatoiron(III) methoxides is presented on the basis of experimental observations for tetraphenylporphinatoiron(III) methoxide.

Experimental

Synthesis of the Metal-free Base of Tetraphenylporphin (H_2TPP). H_2TPP was synthesized by the method of Adler *et al.*[7] Chromatographic purification was repeated on activated alumina columns using chloroform as a solvent and also as an eluent. The elute was concentrated, and then excess methanol was added. Purple needle crystals thus obtained were identified by elemental analysis.

Found: C, 86.18; H, 4.61; N, 8.96%. Calcd for $C_{44}H_{30}N_4$: C, 85.97; H, 4.92; N, 9.11%.

Synthesis of Tetraphenylporphinatoiron(III) Chloride (TPPFe(III)Cl). TPPFe(III)Cl was prepared in dimethylformamide (DMF). H_2TPP (0.3 g) and $FeCl_2 \cdot 4H_2O$ (1.5 g) were dissolved in DMF (200 ml) and refluxed for 3 h. When the solution was cooled, dilute hydrochloric acid were added in small portions. The dark purple crystals thus precipitated were collected by filtration. The complex was recrystallized twice from a mixture of 1,2-dichloroethane and *n*-hexane.

Found: C, 74.94; H, 3.85; N, 7.92; Fe, 7.97; Cl, 5.10%. Calcd for $C_{44}H_{28}N_4FeCl$: C, 75.07; H, 4.01; N, 7.96; Fe, 7.93; Cl, 5.04%.

Synthesis of Tetraphenylporphinatoiron(III) Methoxide (TPPFe(III)OCH_3). A methanol solution of sodium methoxide prepared by dissolving metal sodium (1 g) in dry methanol (100 ml) was added to a solution of TPPFe(III)Cl (0.7 g) in dry benzene (350 ml). The mixture was refluxed for 3 h and then filtered. The filtrate was concentrated under reduced pressure until crystals appeared and then a small amount of dry methanol was added. The blue crystals thus obtained were collected by filtration, washed with dry methanol, and dried *in vacuo* over silica gel.

Found: C, 77.72; H, 4.64; N, 7.87; Fe, 7.91%. Calcd for $C_{45}H_{31}N_4OFe$: C, 77.26; H, 4.47; N, 8.01; Fe, 7.98%.

Synthesis of Bisimidazoletetraphenylporphinatoiron(III) Perchlorate ([TPPFe(III)(Im)$_2$]ClO_4). TPPFe(III)Cl (35 mg) was dissolved in benzene (5 ml). Silver perchlorate (10 mg) was added to the solution. After being refluxed for 4 h, silver chloride was filtered off and then imidazole (6 mg) was added. Reddish purple crystals precipitated upon the addition of imidazole. When the precipitation was completed, unreacted silver perchlorate and imidazole were dissolved by addition of ethyl ether (5 ml). The precipitate thus obtained was dissolved in 1,2-dichloroethane and then filtered for separation of the contaminating silver chloride. The filtrate was condensed under reduced pressure. Benzene was then added for precipitation. Pure crystals were obtained by recrystallization from a mixture of 1,2-dichloroethane and benzene.

Found: C, 66.18; H, 3.67; N, 12.50; Fe, 6.08%. Calcd for $C_{50}H_{36}N_8FeClO_4$: C, 66.42; H, 4.01; N, 12.39; Fe, 6.18%.

Synthesis of μ-Oxo-bis(tetraphenylporphinatoiron(III)) ([TPPFe(III)]$_2$O). The complex was obtained by shaking a benzene solution of TPPFe(III)Cl with aqueous KOH.[8] The resulting benzene solution was evaporated to dryness. The residue was dissolved in chloroform and then methanol was added. The purple crystals thus precipitated were collected and washed with methanol. The complex was purified by chromatography in a column packed with Sephadex LH-20 using tetrahydrofuran as a solvent and an eluent. The first fraction of the elute was evaporated to dryness. The residue was recrystallized from a mixture of 1,2-dichloroethane and *n*-hexane.

Found: C, 77.74; H, 4.07; N, 8.08%. Calcd for $C_{88}H_{56}N_8OFe_2$: C, 78.11; H, 4.17; N, 8.28%.

Measurements of Absorption and Magnetic Circular Dichroism Spectra. The electronic absorption spectra were recorded on a Shimadzu recording spectrophotometer Model MPS-50. Solvents were benzene, and 1,2-dichloroethane purified by fractional distillation using a 1.5 m Dixson-ring packed column and dried by the usual procedure.[9]

The absorption spectra of the powder samples were measured by the opal glass method.[10] Instead of an opal glass plate, a sheet of tracing paper smeared with the solid sample was placed in front of the window of a head-on type photomultiplier in the Shimadzu spectrophotometer.

The circular dichroism under an external magnetic field (MCD) was measured on a JASCO automatic recording spectropolarimeter Model ORD/UV-5 with its CD attachment and electro-magnet. The magnetic field was set at

10000 Gauss.

Magnetic Susceptibility. The magnetic susceptibilities of the complexes were measured at room temperature by means of the Gouy method. After a calibration of the diamagnetic term by the conventional method, the magnetic moments of the complexes were evaluated.[11)]

Infrared Spectra. The infrared spectra of the complexes in KBr disk were taken on a Hitachi infrared spectrometer Model EPI-G3.

ESR Spectra. The ESR spectra were obtained with a Japan Electron Optics Laboratory spectrometer Model JES-ME3X. The static magnetic field was calibrated by means of a proton-resonance gaussmeter.

Results and Discussion

The electronic absorption spectrum of TPPFe(III)Cl is typical of high-spin iron(III) porphyrins. Three other iron(III) porphyins, TPPFe(III)OCH_3, [TPPFe(III)$(Im)_2$]ClO_4 and [TPPFe(III)$]_2$O, exhibit spectra resembling each other, but differing in profile from the spectrum characteristic of high-spin iron(III) porphyrins The absorption and MCD spectra are presented in Figs. 1 and 2.

The absorption spectrum of [TPPFe(III)$(Im)_2$]ClO_4 in 1,2-dichloroethane (Fig. 1) is a typical low-spin spectrum. The low-spin spectrum was also obtained for [TPPFe(III)$(Im)_2$]Cl and [TPPFe(III)$(Im)_2$]ClO_4 in chloroform which consists of ten times or more excess imidazole. La Mar and Walker also observed in their NMR studies that the proton signals of the low-spin species were detected only in the presence of eight times excess imidazole in deuterochloroform.[12)] In chloroform, however, a drift of the absorption spectrum was observed for a few hours even in the presence of excess imidazole. This indicates the dissociation of coordinated imidazole in solution. In 1,2-dichloroethane, the absorption spectrum does not change for a few days after the sample is dissolved in the absence of excess imidazole.

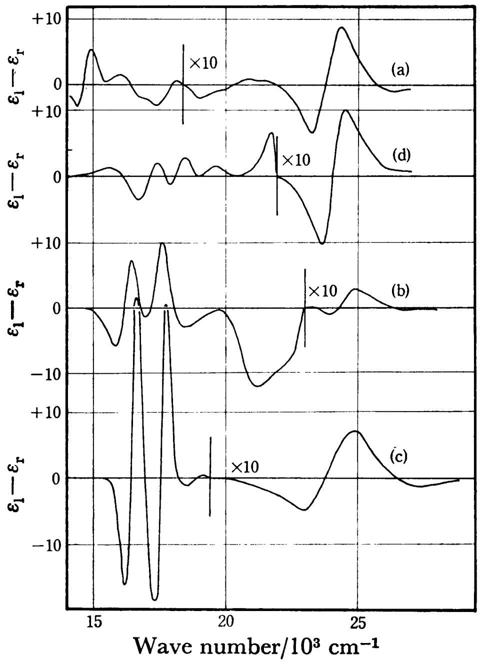

Fig. 2. MCD spectra of TPPFe(III)Cl(a), TPPFe(III)OCH_3(b) and [TPPFe(III)$]_2$O(c) in benzene, and [TPPFe(III)$(Im)_2$]ClO_4(d) in 1,2-dichloroethane.

The absorption spectrum of TPPFe(III)OCH_3 dissolved in dry benzene (Fig. 1) is very similar to that of [TPPFe(III)$(Im)_2$]ClO_4. Unless the solvent and the

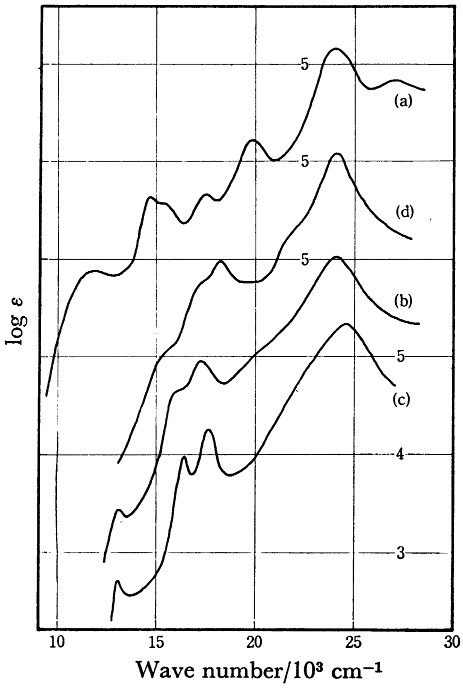

Fig. 1. Absorption spectra of TPPFe(III)Cl(a), TPPFe(III)OCH_3(b) and [TPPFe(III)$]_2$O(c) in benzene, and [TPPFe(III)$(Im)_2$]ClO_4(d) in 1,2-dichloroethane.

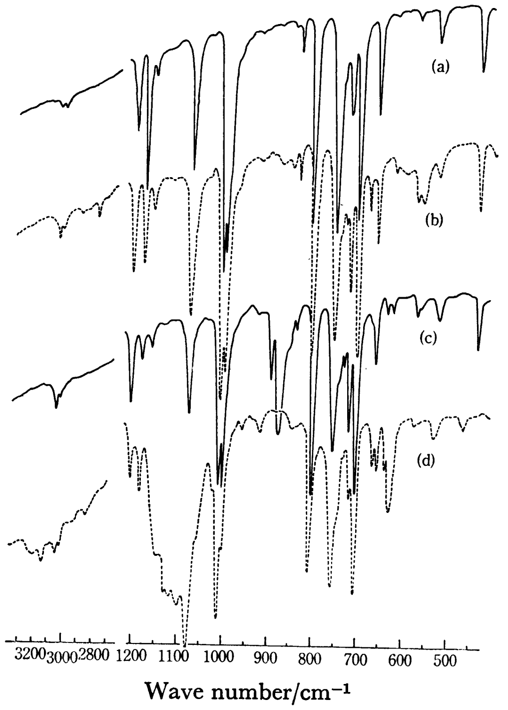

Fig. 3. IR spectra of TPPFe(III)Cl(a), TPPFe(III)OCH_3(b), [TPPFe(III)$]_2$O(c), and [TPPFe(III)$(Im)_2$]ClO_4(d) in KBr disk.

apparatus are sufficiently dried, the absorption spectrum gradually changes to that of [TPPFe(III)]$_2$O. The moisture in solution reacts with TPPFe(III)OCH$_3$ forming [TPPFe(III)]$_2$O, a dimer with Fe–O–Fe bridge.[13] [TPPFe(III)]$_2$O exhibits two strong IR peaks of antisymmetric vibrations of Fe–O–Fe at 875 cm^{-1} and 895 cm^{-1}.[8,13] TPPFe(III)OCH$_3$ lacks such IR peaks in the region but shows a C–H stretching peak of coordinated OCH$_3$ group at 2800 cm^{-1}. The IR spectra are shown in Fig. 3.

TABLE 1. MAGNETIC MOMENTS OF TPPFe(III)Cl, TPPFe(III)OCH$_3$ AND [TPPFe(III)(Im)$_2$]ClO$_4$

Complex	χ (10^{-6} cgs/mol)	Temperature (K)	μ_{eff} (B.M.)	Spin state
[TPPFe(III)(Im)$_2$]ClO$_4$	2493	291.7	2.41	$S=1/2$
TPPFe(III)Cl	14733	292.8	5.87	$S=5/2$
TPPFe(III)OCH$_3$	14489	293.3	5.83	$S=5/2$

The magnetic moments which were measured by the Gouy method are given in Table 1. The measurement reveals that the solid sample of TPPFe(III)OCH$_3$ is in the high spin state $S=5/2$, although the absorption spectrum in benzene is of low-spin type. The ESR spectrum of solid TPPFe(III)OCH$_3$ measured at 77 K ($g_\perp=5.30$, $g_{//}=2.00$) is also a spectrum characteristic of high-spin species such as TPPFe(III)Cl ($g_\perp=6.00$, $g_{//}=2.00$).[14] The ESR spectra are shown in Fig. 4. Since an interconversion of the spin state was possible upon dissolution of the sample into a solvent, the absorption spectra of the solid samples were examined by the opal glass method. They were found, however, to coincide qualitatively with the solution spectra (Fig. 5). A spectral change to be attributed to a spin interconversion does not occur on dissolution. The solution spectrum is less dependent upon solvents unless the solvent molecules replace the axial ligands.

The lowest excited states, which are responsible for the absorption spectra of high-spin iron(III) porphyrins and of high-spin manganese(III) porphyrins, are well described as a configuration-interaction admixture of the lowest triplet and singlet (π, π^*) excited states of porphyrin and the "porphyrin to metal" charge-transfer (CT) excited states.[15] Since the ground state of the high-spin iron(III) porphyrin is $^6A_1$ the allowed photoexcited states should be spin-sextet. The energies of the (π, π^*) excited states $^6E_T(\pm 9a)$, $^6E_T(\pm 1a)$, $^6E_Q(\pm 9b)$ and $^6E_B(\pm 1b)$ and the CT excited states $^6E_{CT}(\pm 5)$ and $^6E_{CT}(\mp 3)$ are given in terms of energy parameters E, K_9, K_1, and E_{CT}.[15] The mixing terms of the excited sextets are given in terms of the delocalization parameter β and the off-diagonal corrections ε, ε', and ε'' for the assumption of an accidental degeneracy in the highest filled porphyrin orbitals. The molecular param-

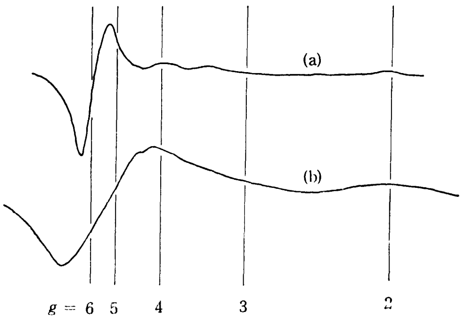

Fig. 4. ESR spectra of TPPFe(III)Cl(a) and TPPFe(III)OCH$_3$(b) in the solid state at 77 K.

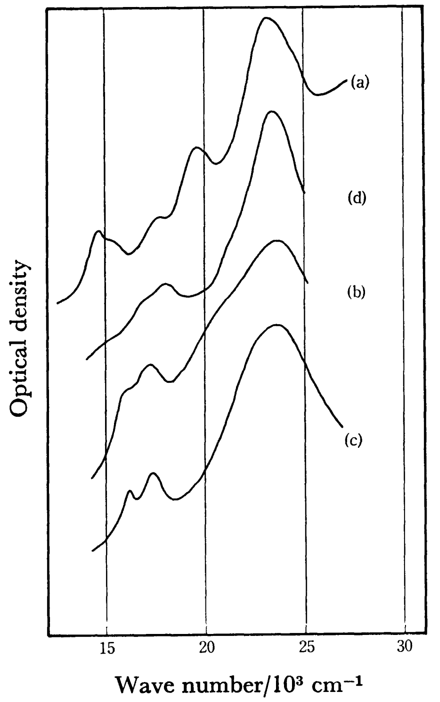

Fig. 5. Absorption spectra of TPPFe(III)Cl(a), TPPFe(III)OCH$_3$(b), [TPPFe(III)]$_2$O(c) and [TPPFe(III)(Im)$_2$]ClO$_4$(d) in the solid state.

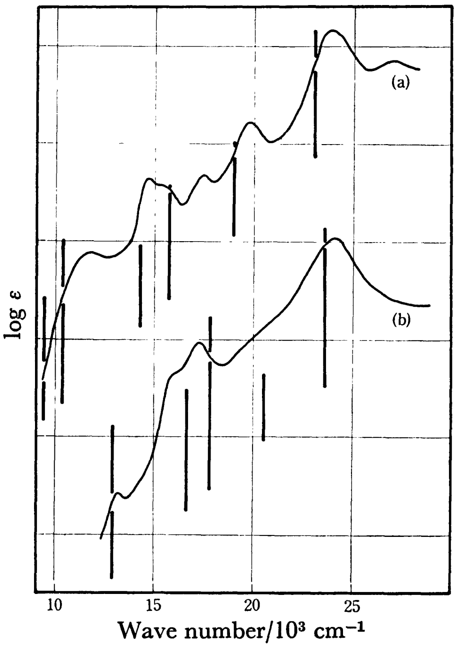

Fig. 6. The calculated lowest excitations of TPPFe(III)Cl(a) ($E_{CT}=12500$ cm^{-1}) and TPPFe(III)OCH$_3$(b) ($E_{CT}=17500$ cm^{-1}). The assumed parameter values are $E=13070$ cm^{-1}, $K_1=4600$ cm^{-1}, $K_9=2730$ cm^{-1}, $\beta=-3000$ cm^{-1}, $\varepsilon=1340$ cm^{-1}, $\varepsilon'=-1340$ cm^{-1}, and $\varepsilon''=0$ cm^{-1}.

TABLE 2. CALCULATED COMPOSITIONS OF THE EXCITED SEXTET STATES OF THE HIGH-SPIN IRON(III) PORPHYRIN (E_{CT}=17500 cm^{-1})

	a^{6}E	b^{6}E	c^{6}E	d^{6}E	e^{6}E	f^{6}E
Excitation energy (cm^{-1})	10700	12800	16700	17800	20400	23500
log ε	2.08	3.02	3.49	4.28	3.67	5.12
$^6E_{CT}$ ($\Lambda_Z=\pm5$)	0.2652	-0.3794	0.5246	0.2326	0.6673	-0.1056
$^6E_{CT}$ ($\Lambda_Z=\mp3$)	0.2541	0.3675	0.0206	0.7899	-0.2382	-0.3453
^6E_T ($\Lambda_Z=\pm9$)	0.6593	-0.5700	-0.4210	-0.0051	-0.2510	0.0150
^6E_T ($\Lambda_Z=\pm1$)	0.6517	0.5980	0.1413	-0.4178	0.1271	0.0810
^6E_Q ($\Lambda_Z=\pm9$)	0.0654	-0.1654	0.7077	-0.0268	-0.6223	0.2823
^6E_B ($\Lambda_Z=\pm1$)	0.0391	0.1058	-0.1610	0.3829	0.1778	0.8850
Λ_Z ($\hbar$)	±4.53	±3.85	±7.52	∓1.27	±6.16	±1.21
Number of the transferred charge	0.135	0.279	0.276	0.678	0.502	0.130

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

eters except E_{CT} were estimated to reproduce the transition energies and the intensity ratio of the Q and B bands of TPPCo(III)Cl in pyridine. The transition energies and intensities for the lowest excited sextets of high-spin iron(III) porphyrins were calculated for a variety of E_{CT}. The calculated lowest excited sextets can well reproduce the observed lowest excited states of TPPFe(III)Cl for E_{CT}=12500 cm^{-1}. The electronic absorption spectrum of TPPFe(III)OCH$_3$ is also reproduced for the same molecular parameters of TPPFe(III)-Cl except a high E_{CT} value of 15000 cm^{-1} or 17500 cm^{-1}. The calculated lowest excited states of TPPFe(III)X are shown with the observed spectra in Fig. 6. In the case of a high-spin iron(III) porphyrin with E_{CT}= 12500 cm^{-1}, the "porphyrin to iron(III)" charge-transfer excited states crucially mix with the lowest triplet (π, π^*) excited states and give rise to a blue shift of the excited state which is essentially assigned to the Q (π, π^*) state. This results in a typical spectrum of high-spin iron(III) porphyrins. In the case of a high-spin iron(III)porphyrin with E_{CT}=17500 cm^{-1}, on the other hand, the charge-transfer excited states do not mix sufficiently with the triplet (π, π^*) excited states, the high-spin iron(III) porphyrin thus exhibiting a spectrum differing from the typical spectrum of high-spin iron(III) porphyrins. Contributions of the composite excited states to each of the lowest excited states are presented in Table 2, together with the calculated values of orbital angular momentum and transferred charge from "porphyrin to iron(III)" in the excited states.

An increase in the charge-transfer energy in high-spin porphyrinatoiron(III) methoxides is attributed to a reduction in the dπ electron affinity of the central iron(III) ion for a greater charge donation by the coordinated OCH$_3$. The magnitude of the zero-field splitting of the $^6A_1$ components of ferric ion ($\Delta E_1 \equiv E(^6A_1 \mp 3/2) - E(^6A_1 \pm 1/2)$) has been directly measured by far-infrared spectroscopy on the methoxide and chloride of ferric deuteroporphyrin-IX dimethyl ester (ΔE_1(OCH$_3$)=9.3 cm^{-1}; ΔE_1(Cl)=17.9 cm^{-1}).[16,17] Here, ΔE_1 is given by $2D$ in terms of $D=\zeta^2/5(E_4-E_6)$, where ζ is the spin-orbit coupling constant and E_4-E_6 is the first-order energy difference between $^4A_2(\theta\xi^2+1-1)$ and $^6A_1(\varepsilon\theta\zeta+1-1)$ states.[18] For a strong axial field, an energy difference between ε and θ is reduced and then $^4A_2$ lies higher. This implies that an increase in the axial ligand field results in a reduction in ΔE_1. Thus the observed zero-field splitting supports a greater charge donation by the coordinated OCH$_3^-$.

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