Synthesis and Magnetic Properties of Octaethylporphyrinatoiron(III) Perchlorate and Its Mono(amine) Adduct. Intermediate-spin State ($S=3/2$) Model for Ferricytochrome c′

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(Received December 26, 1980)

Octaethylporphyrinatoiron(III) perchlorate, its mono(pyridine) and mono(4-substituted pyridine) adducts and bis(tetrahydrofuran)octaethylporphyrinatoiron(III) perchlorate were prepared to mimic the ferricytochrome c′. Magnetic susceptibilities, Mössbauer spectra, and ESR spectra have been measured. Magnetic properties in the crystalline state revealed; (i) Octaethylporphyrinatoiron(III) perchlorate, $OEPFe^{III}ClO_4$ and bis(tetrahydrofuran)octaethylporphyrinatoiron(III) perchlorate, $OEPFe^{III}(THF)_2ClO_4$ are of intermediate-spin state($S=3/2$). (ii) Magnetic susceptibilities and Mössbauer parameters of mono(pyridine) and mono(4-substituted pyridine)octaethylporphyrinatoiron(III) perchlorate, $OEPFe^{III}$(4-X-py)ClO_4 [X=CHO, X=CN, and X=H] are rather similar to those of the low-spin($S=1/2$) states. Absorption spectra showed that octaethylporphyrinatoiron(III) perchlorate is of intermediate-spin state in dichloromethane solution, but of high spin state in acetone solution. Close spectral resemblance of these complexes to the ferricytochrome c′ at physiological pH suggests that the latter is in intermediate-spin state.

Ferrihemoproteins and ferriheme enzymes in general have been classified into two spin-states, that is, the five-coordinated high-spin ($S=5/2$) state and the six-coordinated low-spin ($S=1/2$) state. It is noted that the ferricytochrome c′ isolated from photosynthetic and denitrifying bacteria[1–4] have anomalous magnetic properties defined as intermediate-spin state ($S=3/2$). An unusual electronic spectrum is found in cytochrome c′. The oxidized form[5] in alkaline solution shows a hemichrome spectrum of the low-spin. Below pH 11 the spectrum reverts to a chracteristic of high-spin ferric hemes with split Soret bands. Further change of electronic spectrum is observed as pH decreases. The magnetic moment at physiological condition anomalously shows intermediate values between high-spin and low-spin.[6,7] Mössbauer spectra[8] show large quadrupole splittings which are comparable to those of methemoglobin with the opposite sign.

In order to aid understanding anomalous spin-state, there have been reported few simulations to intermediate-spin complexes by synthetic hemes. In previous communication,[9] we reported briefly syntheses and some magnetic properties of octaethylporphyrinatoiron(III) perchlorate and its mono(amine) adducts. We have described the unusual magnetic moments of these complexes at 288 K as an admixture of the high-spin and low-spin states as follows:

$$^6A_1 \rightleftharpoons {}^2T_2.$$

Since then, two groups have reinvestigated the physicochemical properties of the perchlorate salts of ferric porphyrins. Dolphin and his coworkers[10] reexamined magnetic moments and measured Mössbauer spectra of octaethylporphyrinatoiron(III) perchlorate and bis(ethanol)octaethylporphyrinatoiron(III) perchlorate. They have, however, suggested that these complexes possesses an intermediate-spin iron(III) atom, with the $S=3/2$ at the ground state possibly involving some high-spin character. Scheidt and his coworkers[11] have reported physicochemical properties of diaqua-$\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinatoiron(III) perchlorate and perchlorate-$\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinatoiron(III). We have studied crystal structure of the perchlorate complex[12] and its paramagnetic ^{1}H-NMR spectra in organic solvents.[13] In a previous communication,[9] we also reported the first syntheses of mono(amine) adducts and their magnetic moments at room temperature. We wish to report here elaborate measurements on magnetic susceptibilities, Mössbauer spectra, and ESR spectra of octaethylporphyrinatoiron(III) perchlorate, and three mono(amine) adducts in solid state.

Experimental

Preparation of Compounds. Ocatethylporphyrinatoiron(III) Perchlorate [$OEPFe^{III}ClO_4$] (1): To 500 mg of $OEPFe^{III}$-Cl[14] in benzene (200 ml) was added 500 mg of anhydrous silver perchlorate and the solution was refluxed gently for 1 h. The hot solution was filtered and then allowed to stand overnight at room temperature. The resultant needle crystals (450 mg) were collected, washed with petroleum ether and dried under vacuum. Bis(tetrahydrofuran)octaethylporphyrinatoiron(III) perchlorate [$OEPFe^{III}(THF)_2$-ClO_4] (**2**). To 100 mg of **1** in dichloromethane (20 ml) was added tetrahydrofuran (10 ml). The solution was warmed for 15 min and allowed to come to room temperature. The crystals were collected, washed with tetrahydrofuran, and dried under vacuum (95 mg).

(4-Formylpyridine)octaethylporphyrinatoiron(III) Perchlorate [$OEPFe^{III}$(4-CHO-py)ClO_4] (3): To 100 mg of **1** in dry benzene (100 ml) was added 0.5 ml of 4-formylpyridine. The solution was refluxed for 2 h, condensed to a small volume and allowed to stand overnight at room temperature. The resulting dark brown crystals were filtered, washed with petroleum ether and dried under vacuum (90 mg).

(4-Cyanopyridne)octaethylporphyrinatoiron(III) Perchlorate [$OEPFe^{III}$(4-CN-py)ClO_4] (4): The preparative method is identical with that described above. The dark brown crystals (95 mg) were obtained from 100 mg of **1**.

(Pyridine)octaethylporphyrinatoiron(III) Perchlorate [$OEPFe^{III}$-(py)ClO_4] (5): To 100 mg of **1** in dry benzene (100 ml)

		C (%)		H (%)		N (%)	
		Calcd	Found	Calcd	Found	Calcd	Found
(1)	$C_{36}H_{44}N_4O_4ClFe$	62.84	62.94	6.45	6.48	8.14	8.04
(2)	$C_{44}H_{60}N_4O_6ClFe$	63.50	63.45	7.27	7.26	6.73	6.79
(3)	$C_{42}H_{49}N_5O_5ClFe$	63.44	63.36	6.21	6.28	8.81	8.89
(4)	$C_{42}H_{48}N_6O_4ClFe$	63.67	63.40	6.10	6.26	10.61	10.32
(5)	$C_{41}H_{49}N_5O_4ClFe$	64.19	64.33	6.44	6.34	9.13	8.95

was added 0.5 ml of pyridine and the solution was refluxed for 20 min. The deep red precipitates were collected, washed with benzene, and dried under vacuum (95 mg). The results of elemental analyses are tabulated above.

Magnetic and Spectral Measurements. *Magnetic Susceptibilities*: A Faraday magnetic balance was employed for measurements of magnetic susceptibilities from 77 K to 300 K. The magnetic susceptibilities of anhydrous hexaammine-chromium chloride powder was used as a "thermometer" which was calibrated at each run to an atmospheric liquid nitrogen temperature with corrections for the Hg-barometer and gravitational constant following the procedure of Linder.[15] The accuracy for the measurements was not less than 10%. The diamagnetic susceptibilities of porphyrin ligand and axial ligands were corrected by measurement of free base octaethylporphyrin and by Pascal's rule.

Mössbauer Spectra: Mössbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. The velocity scale was calibrated absolutely from an independent Mössbauer run using a thin metallic iron absorber and the center of symmetry of the spectrum was taken as zero velocity. The velocity was determined to an accuracy of ± 0.01 mm/s.

ESR Spectra: The ESR spectra of polycrystalline sample and in dichloromethane glass were measured at 77 K and at 293 K by using a JEOL X-band spectrometer.

Results

Figure 1 shows effective magnetic moments of **1**, **2**, **3**, **4**, and **5** at various temperatures from 77 K to 270 K. The effective magnetic moments of **1** and **2** are lower than those of typical high-spin state (5.9 BM) and higher than typical low-spin state (2.15—2.72 BM).[16] On the other hand, for mono(amine) adducts, **3**, **4**, and **5**, the effective magnetic moments vary greatly with the kinds of substituent at 4-position of pyridine. The effective magnetic moments of mono(pyridine) adduct **5** and mono(4-cyanopyridine) adduct **4** are closely similar to the six-coordinated low-spin complexes[16] at low temperature, but at high temperature these values become larger than those of low-spin complexes. It is noted that the magnetic moments of the 4-formyl pyridine adduct **3** are larger than those of mono(amine) adducts **4** and **5**, but smaller than those of the perchlorates **1** and **2**.

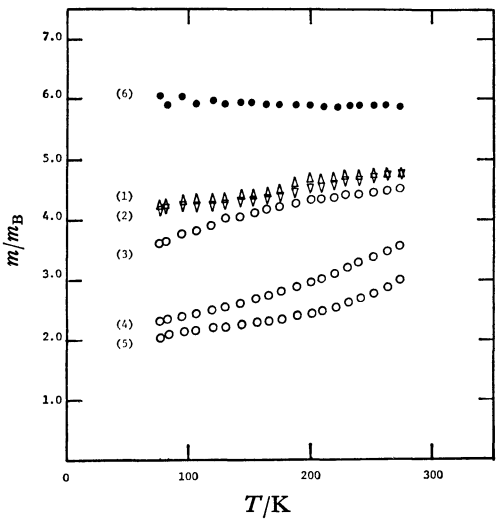
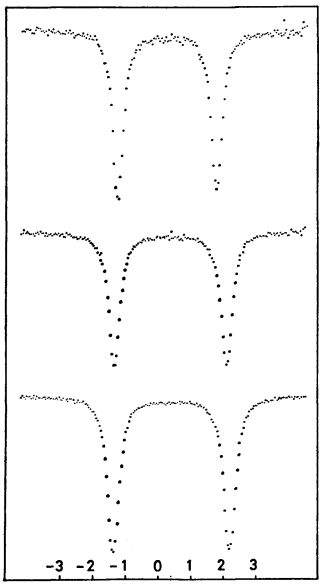


Fig. 1. Effective magnetic moments *versus* temperatures. (1): OEPFe(III)ClO_4, (2): OEPFe(III)$(THF)_2ClO_4$, (3): OEPFe(III)(4-CHO-py)ClO_4, (4): OEPFe(III)-(4-CN-py)ClO_4, (5): OEPFe(III)(py)ClO_4, (6): OEPFe(III)SCN.

Table 1 summarizes the Mössbauer parameters, isomer shifts δ (mm/s) and quadrupole splitting ΔE_Q (mm/s) of complexes at various temperatures. The isomer shifts of all these complexes are in the range of 0.2—0.4 mm/s, indicating typical iron(III) state. On the other hand, the quadrupole splittings of **1** and **2** show 3.14 and 3.08 mm/s at room temperature, respectively. These values are very large compared with those of usual iron(III) complexes and identical with those reported by Dolphin and his coworkers.[10] Mono(amine) adducts **3**, **4**, and **5** have smaller quadrupole splittings than the complexes **1** and **2**. In particular Mössbauer parameters of the mono(pyridine) adducts **3**—**5** are close to those of the six-coordinated low-spin complexes.[16] As shown in Figs. 2—6, high velocity lines of the complexes **4** and **5** are broadened at lower temperatures. Therefore, the sign of the quadrupole coupling can be determined to be positive. In the case of mono(4-formylpyridine) adduct **3**, the line broadening at high velocity due to the

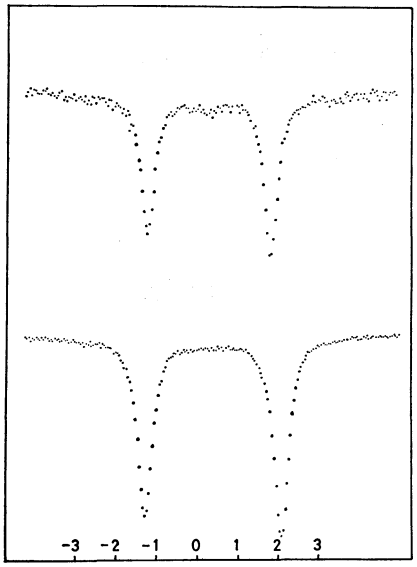
Table 1. Mössbauer parameters

	Compound	T/K	ΔE_Q/mm s^{-1}	δ/mm s^{-1}
1	OEP·Fe(III)·ClO_4	RT	3.14	0.31
		77	3.57	0.39
		4.2	3.54	0.40
2	OEP·Fe(III)·	RT	3.04	0.31
	$(THF)_2$·ClO_4	77	3.34	0.42
3	OEP·Fe(III)·	RT	2.29	0.30
	(4-CHO-py)·ClO_4	77	2.35	0.38
		4.2	2.22	0.40
4	OEP·Fe(III)·	RT	2.34	0.27
	(4-CN-py)·ClO_4	77	2.05	0.25
		4.2	relax.	
5	OEP·Fe(III)·	RT	1.96	0.21
	(py)·ClO_4	77	1.95	0.27
		4.2	1.94	0.27



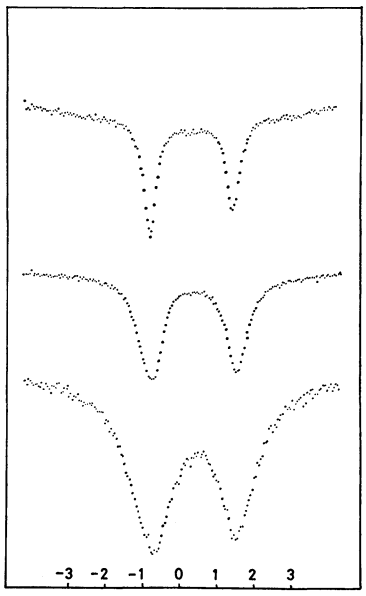
Velocity/mm s^{-1}

Fig. 2. Mössbauer spectra of OEPFe(III)ClO_4 at RT, 77 K, and 4.2 K.



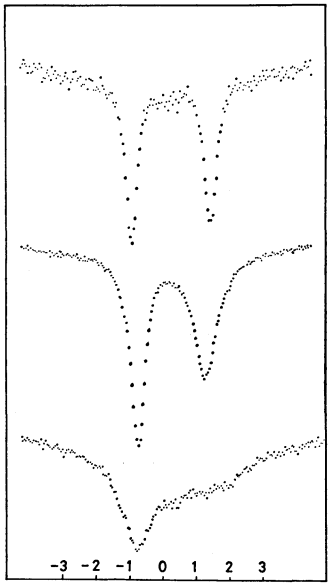
Velocity/mm s^{-1}

Fig. 3. Mössbauer spectra of OEPFe(III)$(THF)_2ClO_4$ at RT and 77 K.



Velocity/mm s^{-1}

Fig. 4. Mössbauer spectra of OEPFe(III)(4-CHO-py)ClO_4 at RT, 77 K, and 4.2 K.



Velocity/mm s^{-1}

Fig. 5. Mössbauer spectra of OEPFe(III)(4-CN-py)-ClO_4 at RT, 77 K, and 4.2 K.

relaxating is much smaller than the other two mono-(amine) adducts even at 4.2 K.

ESR spectra of these complexes in solid state at 293 and 77 K are shown in Figs. 7 and 8, respectively, and observed g-values are summarized in Table 2. Complexes **1** and **2** show very broad signals at around $g=4$ at room temperature. On the other hand the mono(amine) adducts **3**, **4**, and **5** show also broad signals at $g=4.41$, 3.75, and 2.40 with very weak peaks around $g=2$, respectively. The line shapes and g-values of these complexes at room temperature are very much different from those of ordinary high-spin or low-spin iron(III) complexes hitherto reported. For mono(pyridine) adduct **5**, the signal at $g=2.06$ seems to be contaminated by organic radical species. The ESR spectra at 77 K were remarkably different from those at room temperature as shown in Fig. 8. The complex **2** shows still one broad signal at $g=4.61$ in solid state, but anisotropic g-values at $g=4.68$ and 2.00 in dichloromethane glass. The complex **1** shows a pair of anisotropic g-values at 5.83 and 1.48. On the other hand, three mono-(amine) adducts exhibit similar spectra with a pair of anisotropic g-values at low temperature, although the g-values are slightly different from each other. The g-values are markedly changed from 4.69 to 5.40 upon introduction of the formyl group at the 4-position of pyridine. The ESR spectra of **1** and **2** at 77 K show entirely different signals from those of

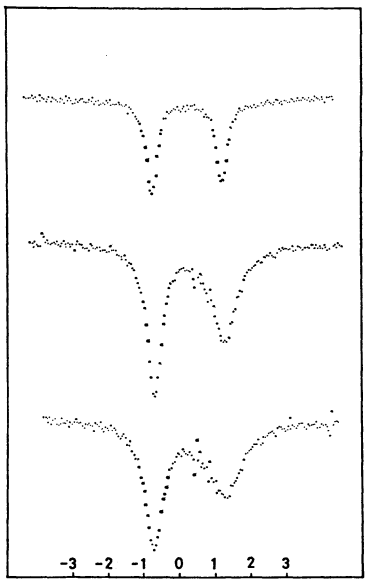


Fig. 6. Mössbauer spectra of OEPFe(III)(py)ClO_4 at RT, 77 K, and 4.2 K.

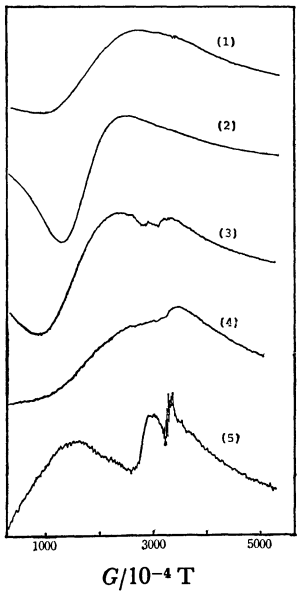


Fig. 7. ESR spectra at RT.
(1): OEPFe(III)ClO_4, (2): OEPFe(III)$(THF)_2ClO_4$, (3): OEPFe(III)(4-CHO-py)ClO_4, (4): OEPFe(III)-(4-CN-py)ClO_4, (5): OEPFe(III)(py)ClO_4.

usual high-spin or low-spin complexes of ferric porphyrin. The ESR spectra of mono(amine) adducts **3**, **4**, and **5** exhibit the strong broad signals at high *g*-values(lower magnetic field) and the maximum absorption (zero derivative) is shifted towards lower *g*-values(higher magnetic field).

Absorption spectrum of the complex **1** changes remarkably with polarity of solvent as shown in Fig. 9. In acetone the complex **1** exhibits a spectral characteristic of the high-spin complexes, whereas in dichloromethane the Soret band is largely broadened and slightly splitted. The band at 630 nm assigned to a charge transfer band is shifted to longer wave length (636 nm) in dichloromethane than in acetone (628 nm).

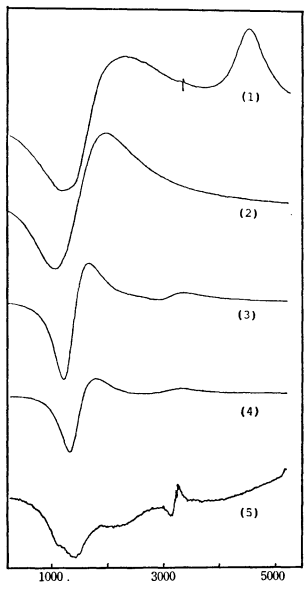


Fig. 8. ESR spectra at 77 K.
(1): OEPFe(III)ClO_4, (2): OEPFe(III)$(THF)_2ClO_4$, (3): OEPFe(III)(4-CHO-py)ClO_4, (4): OEPFe(III)-(4-CN-py)ClO_4, (5): OEPFe(III)(py)ClO_4.

Table 2. ESR parameters

	RT		77 K	
	$g_{//}$	$g_\perp$	$g_{//}$	$g_\perp$
1 OEP·Fe(III)·ClO_4	3.9		1.5	5.8
2 OEP·Fe(III)·$(THF)_2$·ClO_4	3.9		4.6 2.0	 4.7[a]
3 OEP·Fe(III)·(4-CHO-py)·ClO_4	2.1	4.4	1.7	5.4
4 OEP·Fe(III)·(4-CN-py)·ClO_4	2.0	3.8	2.0	5.0
5 OEP·Fe(III)·(py)·ClO_4	2.1	2.4	2.5	4.7

	7 K	
	$g_{//}$	$g_\perp$
ESR spectral state A	1.99	4.77[20]
Protein state B_1	2.02	5.94[20]
Protein state A_1	1.99	4.75[20]
Protein state A_2	1.99	5.27[20]
Protein state B_2	2.00	5.68, 6.14[20]
Acid metmyoglobin	2.01	5.92[b]

a) Measured in dichloromethane glass. b) J. Peisah, W. E. Blumberg, S. Ogawa, E. A. Rachmilewitz, and R. Oltzik, *J. Biol. Chem.* **246**, 3342—3355 (1971).

Discussion

The complex **1** showed effective magnetic moments μ_{eff}=4.2 BM at 77 K and 4.7 BM at 275 K. Then these values are compared with calculated spin only values μ_{eff}=5.92, 3.87, and 1.73 BM for S=5/2, 3/2, and 1/2, respectively. The complexes **1** and **2** can be

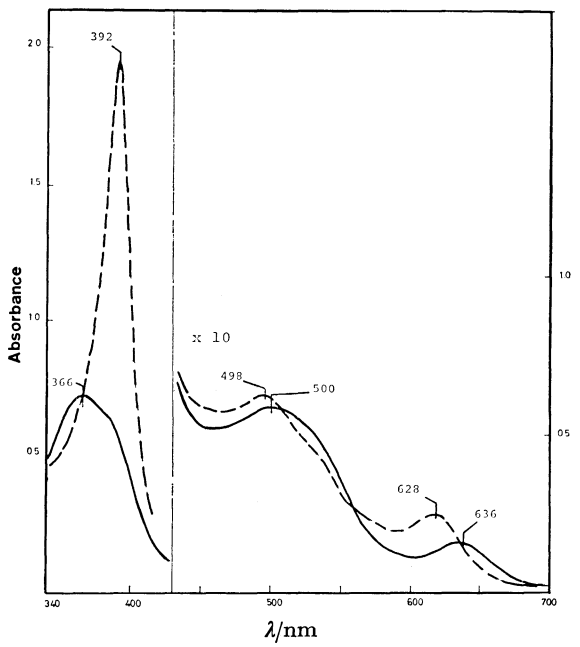


Fig. 9. Absorption spectra of $OEPFe(III)ClO_4$, (——) in CH_2Cl_2 and (----) in acetone.

regarded as intermediate-spin complexes. Harris has predicted a possible existence of pure quartet ground state ($S=3/2$) on theoretical consideration by using a strong crystal field model.[17] The ESR signals in the tetragonal symmetry might have only one transition between the exited state doublets with $g=2$ and 4. The intensity of this transition should be temperature dependent and also should vary with extent of spin-orbital coupling.[18] In fact the complexes **1** and **2** give a very broad signal at about $g=3.9$ as shown in Fig. 7, whose patterns are very similar to that of iron(III) bis(thiocarbamates) characterized as an intermediate-spin complex.[16] At low temperature, the complex **1** has some anisotropic character so that g-value at around 4 seems to split into the two values $g=5.83$ and 1.48, as shown in Fig. 8. On the other hand, the complex **2** in solid state has no anisotropic character even at 77 K, but in dichloromethane glass it gives anisotropic g-values at 4.68 and 2.00. The Mössbauer spectra of the complexes **1** and **2** did not show any relaxation broadning, as mentioned by Dolphin and his coworkers, suggesting fast spin relaxation between both $|\pm 1/2>$ and $|\pm 3/2>$ doublets. Comparison of the magnetic susceptibilities, the ESR spectra and the Mössbauer spectra leads us to conclude that the complexes **1** and **2** are of intermediate-spin state.

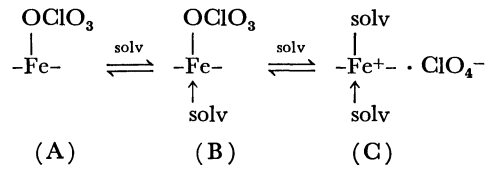
Mono(amine) adducts **3**, **4**, and **5** have effective magnetic moments between the low-spin and the intermediate-spin states. The ESR spectra of these compounds give anisotropic g-values at $g=5.47$—4.67 and $g=1.70$—2.05 at 77 K. In particular, the magnetic moments and Mössbauer parameters of the mono(pyridine) adduct **5** indicate that the spin state of **5** at low temperature is essentially low-spin state. However, the ESR spectrum of **5** is different from that of the hexa-coordinated low-spin complex. This fact suggests that mono(amine) adducts do not exist in pure low-spin state, but in a mixed spin state with low-spin($S=1/2$) and intermediate-spin($S=3/2$) states. Small differences in the magnetic properties among them may be attributed to the extent of admixture of two spin states. Weight of the quartet state in the mixed spin state increases in the following order, **3**>**4**>**5**. Magnetic properties of the 4-formylpyridine adduct **3** are very close to those of the complex **1**. Also magnetic properties of the mono(amine) adducts are consistent with the theoretical prediction for a quartet-doublet mixed spin iron(III) ion by Harris.[17] The effective magnetic moments of ferricytochrome c′ at pH 7[20] have been reported to be 5.15 BM at 293 K and 3.4 BM at 2.8 K. Ferricytochrome c′ shows anomalous feature in the ESR parameters and the shape of the Soret band in absorption spectrum. The ferricytochrome c′ at physiological pH exhibits a strong ESR absorption at high g-value $g=4.77$ and a weaker one at $g=1.99$.[20] The former absorption is much broadened and its maximum absorption (zero derivative) is shifted toward lower g-values than ferrimyoglobin and ferrileghemoglobin.[7] Maltempo has described unusual properties of ferricytochrome c′ by assuming that the electronic comfiguration of hemin at the ground state consists of substantial quantum mechanical admixture of intermediate-spin($S=3/2$) and high-spin($S=5/2$) states, coupled *via* the spin-orbit interaction. Therefore, intermediate spin complexes **1** and **2** seem to be good models for ferricytochrome c′ at physiological pH.

Present results lead us to postulate that a histidyl imidazole coordinates weakly to the iron(III) atom of ferricytochrome c′ even at physiological pH. Therefore, the mono(amine) adducts rather than complexes **1** and **2** are better model complexes for the ferricytochrome c′.

As is seen in Figs. 7 and 8, the mono(amine) adducts can duplicate unusual ESR specturm of ferricytochrome c′. The g-values of ferricytochrome c′ at the various conditions are referred in Table 2. Comparison of its g-values with model compounds suggests that the ground state of the ferricytochrome c′ at low temperature is similar to those of the mono(amine) adducts. Histidyl imidazole is considered to be most probable axial ligand to the heme in the enzyme. Analysis of amino acid sequence of apocytochrome c′ rationalizes possible ligation of the histidyl imidazole as fifth axial ligand.[21] There are, however, so many candidates of the sixth ligand such as water, aspartic acid, glutamic acid, and lysine.[22] On the basis of physicochemical properties of model complexes, it is proposed that relatively weak ligand coordinates to the hemin in cytochrome c′, and the bonding between iron atom and sixth ligand has more ionic character than that of the ferric hemoproteins. Positive charge seems to be localized on the iron(III) atom relative to the penta-coordinate ferric high-spin state. As is stated by Strekas and Spiro,[23] the differences of energy levels between d_π orbital and d_{z^2} or d_{z^2} and $d_{x^2-y^2}$ orbitals are very sensitive to the nature of axial ligands. Spin state of ferric porphyrin complex is markedly dependent on strength of axial ligation of the fifth and sixth ligands. Coordination of the histidyl

imidazole seems to be strongly influenced by changes in environment near proximity of the heme, which are induced by pH and temperature. Extensive investigations on the ferric porphyrin complex conclude that spin state is generally determined by coordination numbers of axial ligands. Namely it has been believed that the high-spin state and low-spin state constitute the five-coordinated complex of square pyramidal structure and the six-coordinated complexes of octahedral structure, respectively. We have found new iron(III) complexes having anomalous spin-state and coordination numbers, when a weak field ligand such ClO_4^- was employed.[13] Recently LaMar[24] and Scheidt's[11] groups have pointed out the existence of the six-coordinated high-spin species in the solution or in crystalline state.

Visible spectrum of ferricytochrome c′ shows absorptions at 400, 490, and 632 nm.[25] The absorption at 632 nm is explained as a charge transfer band. There is no essential difference between the electronic structure of d_π-orbital for intermediate spin($S=3/2$) and high spin($S=5/2$). Absorption spectra of **1** in CH_2Cl_2 and solid state can duplicate that of the oxidized form of cytochrome c′. Penta-coordinated iron(III) complex **1** shows remarkable solvent effect on electronic spectrum.[13] Axial ligation of polar solvent molecule results in formation of asymmetric hexa-coordinated (B) and symmetric hexa-coordinated iron(III) complex(C). The complex **2** is defined as the



(A) (B) (C)

solv: solvent molecule

type (C). New hexa-coordinated complexes **3**—**5** constitute asymmetric coordinated complex at axial fifth and sixth sites. Addition of strong basic ligand such as imidazole to the hemin affords bis(imidazole) adduct. Consequently, spin state of the hemin is sensitive to coordination of axial ligand and delocalization of positive charge. These two factors are very important in biological systems. The spin state of the prosthetic heme in hemoproteins is determined by axial ligation of the residue of amino acid and polarity near proximity of the heme.

From present results, we are enforced to support that the ground state electronic configuration of the ferricytochrome c′ at physiological pH is of substantial quantum mechanical admixture of quartet and sextet states. Furthermore, a possibility of an admixture of quartet and doublet states is also proposed for the ferricytochrome c′ at low temperature.

This work was partially supported by a Grant-in-Aid for Special Project Research No. 511311 from Ministry of Education, Science and Culture.

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