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ESR Studies of A_{1u} and A_{2u} Oxoiron(IV) Porphyrin π-Cation Radical Complexes. Spin Coupling between Ferryl Iron and A_{1u}/A_{2u} Orbitals

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This study shows the ESR spectra of oxoiron(IV) porphyrin π-cation radicals of **1**−**8** in dichloromethane−methanol (5:1) mixture. We reported in a previous paper that oxoiron(IV) porphyrin π-cation radicals of **1**−**4** are in an a_{1u} radical state while those of **5**−**8** are in an a_{2u} radical. The ESR spectra ($g_\perp^{\mathrm{eff}} \sim 3.1$ and $g_\parallel^{\mathrm{eff}} \sim 2.0$) for the a_{1u} radical complexes, **1**−**4**, appear quite different from those reported previously for the oxoiron(IV) porphyrin π-cation radical of **5** ($g_y = 4.5$, $g_x = 3.6$, and $g_z = 1.99$). The unique ESR spectra of the a_{1u} radical complexes rather resemble those of compound I from *Micrococcus lysodeikticus* catalase (CAT) and ascorbate peroxidase (ASP). This is the first examples to mimic the ESR spectra of compound I in the enzymes. From spectral analysis based on a spin Hamiltonian containing an exchange interaction, the ESR spectra of **1**−**4** can be explained as a moderate ferromagnetic state ($J/D \sim 0.3$) between ferryl $S = 1$ and the porphyrin π-cation radical $S' = {}^1/_2$. The magnitudes of zero-field splitting (D) for ferryl iron and isotropic J value, estimated from the temperature-dependence of the half-saturation power of the ESR signals, are $\sim$28 and $\sim$+8 cm^{-1}, respectively. A change in the electronegativity of the β-pyrrole substituent hardly changes the ESR spectral feature while that of the meso-substituent slightly does owing to the change in the E/D value. On the basis of the present ESR results, we propose the a_{1u} radical state for compound I of CAT and ASP.

Introduction

An oxoiron(IV) porphyrin π-cation radical species has been identified in catalytic cycles of some peroxidases,[1] catalases,[2] and cytochrome P-450s.[3] For peroxidases and catalases,[4] the oxoiron(IV) porphyrin π-cation radical has been known as a reactive intermediate called compound I, and compound I has been also proposed for the reactive oxygenating intermediate of cytochrome P-450.[3] For over a decade, because of the importance in biological functions, the electronic states of compound I have been studied by electronic absorption,[4,5] NMR,[6] resonance Raman,[7] ENDOR,[8] MCD,[9] Mössbauer,[10] and EXAFS[11] spectroscopies. ESR studies of compound I have also been performed for several peroxidases. The ESR spectrum of compound I of horseradish peroxidase (HRP) showed a broad signal around $g \sim 2.0$[12] while that of chloroperoxidase (CPO) exhibited signals at $g \sim 2.0$ and 1.7.[13] A detailed study explained these difference in terms of magnetic interaction: very weak magnetic interaction for HRP and moderate antiferromagnetic interaction for CPO.[12,14] More recently, quite unique ESR spectra have been reported for the compound I of *Micrococcus lysodeikticus* catalase (CAT)[15] and ascorbate peroxidase (ASP).[16] Theoretical analysis suggested moderate ferromagnetic interaction for these compound I. Although a variety of ESR spectra and magnetic interactions have been reported for compound I, there is no explanation of the relation between the magnetic interaction and its electronic ground state, e.g., the a_{1u}/a_{2u} states.

To answer this question, ESR studies of model complexes have been carried out in many laboratories. Oxoiron(IV) porphyrin π-cation radical complex was first prepared by Groves et al. in the reaction of chloroiron(III) *meso*-tetramesitylporphyrin (TMP) with *m*-chloroperoxybenzoic acid (mCPBA) at −80 °C.[17] The complex exhibited a typical $S = {}^3/_2$ ESR spectrum ($g_y = 4.5$, $g_x = 3.5$, and $g_z = 1.98$)[18] that is quite different from those reported in the enzyme systems. The study combined with Mössbauer measurements revealed a strong

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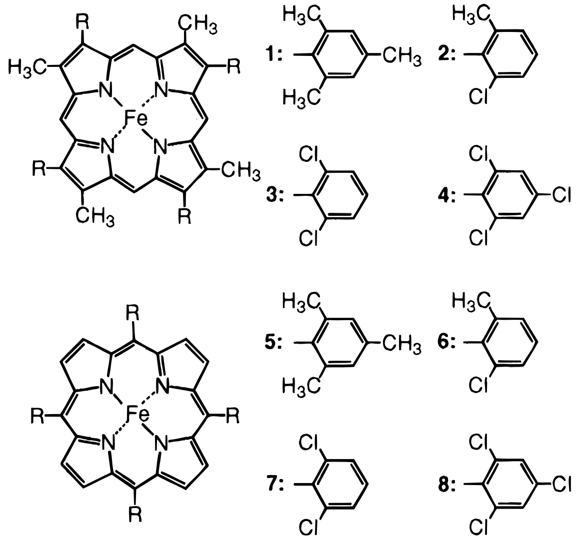

Figure 1. Structures of the porphyrin core of various substituted iron porphyrin complexes (**1**−**8**) employed in this study. Axial ligands were omitted in this figure.

ferromagnetic interaction between iron(IV) $S = 1$ and the porphyrin π-cation radical $S = {}^1/_2$ spins.[18,19] Later, a similar $S = {}^3/_2$ ESR spectrum was also reported for an oxoiron(IV) porphyrin π-cation radical complex having a 2,6-dichlorophenyl group at the meso position.[20] Although ESR spectra of several oxoiron(IV) porphyrin π-cation radical complexes have been reported, there has not been a model complex that can mimic the ESR spectral features of the compounds I in enzymes.

In this paper, we report an ESR study of oxoiron(IV) porphyrin π-cation radical complexes of **1**−**8**, shown in Figure 1. Recently, we have reported the absorption spectral and NMR studies of oxoiron(IV) porphyrin π-cation radical complexes of **1**−**8** and showed that the complexes of **1**−**4** have an a_{1u} radical state while those of **5**−**8** have an a_{2u} radical state.[21] We show here that the a_{1u} radical complexes of **1**−**4** can first mimic the ESR spectra of compound I of CAT and ASP while the a_{2u} radical complexes of **5**−**8** exhibit typical $S = {}^3/_2$ ESR spectra. The spectral analysis clearly shows the characteristics of spin couplings for the a_{1u} and a_{2u} radical complexes: a moderate ferromagnetic coupling for the a_{1u} complex and a strong ferromagnetic coupling for the a_{2u} complex. On the basis of present results, we discuss the orbital symmetry of the porphyrin radical and the magnetic interaction for compound I.

Experimental Section

Materials. Dichloromethane was refluxed over calcium hydride for 3 h and then distilled. Methanol and *m*-chloroperoxybenzoic acid (mCPBA) were purchased from Nacalai Tesque and used without further purification. 2,7,12,17-Tetramethyl-3,8,13,18-tetraarylporphyrins, **1**−**4**, were synthesized by the previous method.[21a,22] 5,10,15,20-Tetraarylporphyrins, **5**−**8**, were prepared by the method described in the literature.[21a,23] Iron was inserted into the porphyrins by refluxing in acetic acid with iron(II) chloride and sodium acetate, and the iron(III) complex was purified using an alumina column. Chloroiron(III) porphyrins were prepared from the reaction of hydroxyiron(III) porphyrins with dilute HCl solution. Absorption spectra of chloroiron(III) complexes of **1**−**8** were identical with those in the previous report.[21a] Perchlorate iron(III) porphyrins of **1**−**8** were synthesized by the reaction of chloroiron(III) porphyrins with silver(I) perchlorate in dichloromethane.[24]

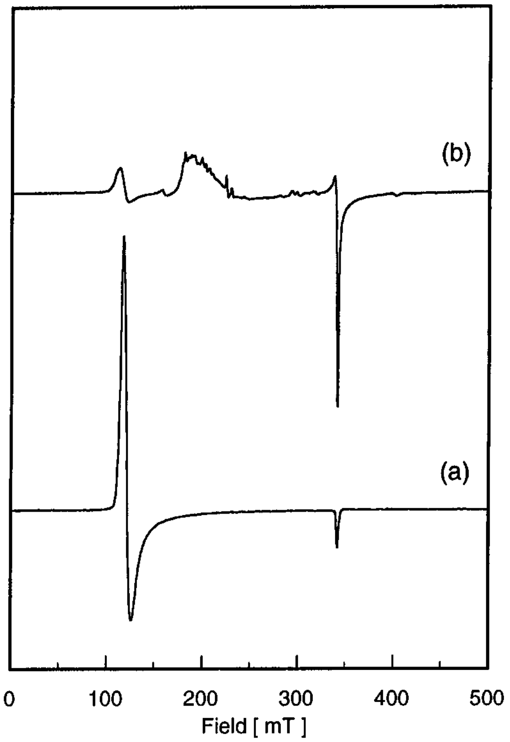

Figure 2. ESR spectra of the perchlorate iron(III) porphyrin of **1** (a) and its oxoiron(IV) porphyrin π-cation radical complex (b) formed from the reaction with mCPBA. (a) Conditions: sample concentration, 3 mM in dichloromethane−methanol (5:1); temperature, 4 K; microwave frequency, 9.471 GHz; microwave power, 5.13 μW; time constant, 82 ms; gain, 6.3×10^3. (b) Conditions were as in part a except the complex and mCPBA concentrations were 2 mM; microwave power was 0.513 mW; and the gain was 2.0×10^3.

Physical Measurements. ESR spectra were recorded on a JEOL TE-200 equipped with an Air Products liquid helium cryostat and a Bruker ESP-300 equipped with an Oxford liquid helium cryostat. The magnetic field was calibrated by an Echo Electronics NMR field meter EMF-2000A.

ESR Samples. Oxoiron(IV) porphyrin π-cation radical complexes were prepared in an ESR sample tube. The iron(III) perchlorate complex (2−4 mM) in a dichloromethane−methanol mixture (5:1) was placed into an ESR tube, and the solution was cooled to −80 °C in a methanol-liquid nitrogen bath. mCPBA (1−1.2 equiv) in dichloromethane was slowly added to the solution. After the solution color changed to green, the solution in the ESR tube was immediately frozen to 77 K and was subjected to ESR measurements.

Results

ESR Spectra of A_{1u} Radical Complexes. Figure 2 shows the ESR spectra of the iron(III) perchlorate complex and oxoiron(IV) porphyrin π-cation radical complex of **1** in dichloromethane−methanol (5:1) at 4 K. The ESR spectrum of the iron(III) perchlorate complex of **1** exhibits signals at $g = 5.6$ and 2.0 (Figure 2a). On addition of 1.2 equiv of mCPBA, the signals almost disappeared and new signals are observed at *g*

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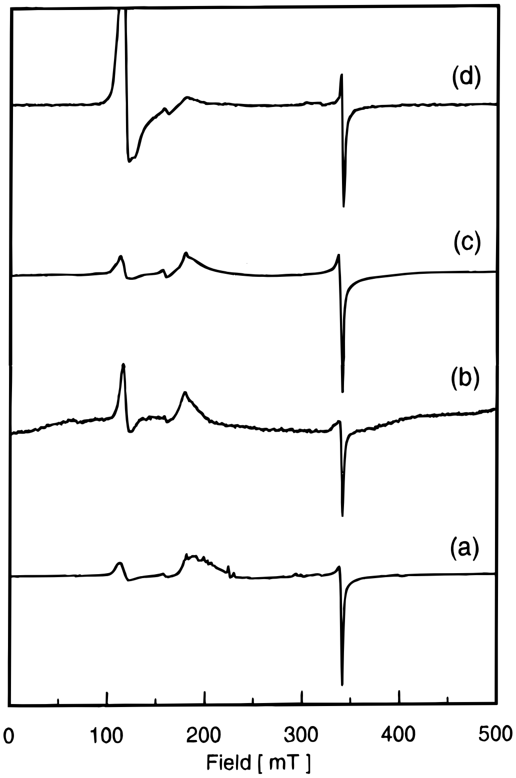

Figure 3. ESR spectra of oxoiron(IV) porphyrin π-cation radical complexes of **1**−**4** in dichloromethane−methanol (5:1). Conditions: sample concentrations, 1−3 mM; temperature, 4 K except 10 K for **3**; microwave frequency, 9.47 GHz; microwave power, 0.5−1 mW; time constant, 82 ms; gain, 5×10^2 to 1×10^4. Key: (a) **1**; (b) **2**; (c) **3**, (d) **4**.

$= 3.6$ and $g = 1.98$, in addition to the signal at $g = 4.3$ arising from decomposed heme compound (Figure 2b).[25] When excess mCPBA was added, we observed an increase in intensity of the $g = 4.3$ signal and a sharp free radical signal around $g = 2.0$, suggesting that the porphyrin ring was decomposed by excess mCPBA. The ESR spectrum of the oxoiron(IV) porphyrin π-cation radical of **1** is quite unique, and the spectral feature is totally different from that of TMP that exhibited a typical $S = {}^3/_2$ ESR spectrum with $g_y = 4.5$, $g_x = 3.5$, and $g_z = 1.98$.[18] The ESR spectrum of the oxoiron(IV) porphyrin π-cation radical of **1** rather resembles that of compound I of ASP and CAT.[15,16] Theoretical analysis of the present ESR spectrum of **1** suggests a moderate ferromagnetic interaction between the ferryl iron and the radical spins. The details will be discussed in the Discussion.

To investigate the effect of the electronegativity of the β-pyrrole substituent on the ESR spectral features, we measured the ESR spectra of the oxoiron(IV) porphyrin π-cation radical complexes of **2**−**4**. The ESR spectra are shown in Figure 3, and the g values are summarized in Table 1. The ESR spectra of **2**−**4** are almost similar to that of **1**, i.e., a broad signal around $g \sim 3.6$ and a sharp signal around $g \sim 1.98$.[25] The present ESR spectra suggest that the oxoiron(IV) porphyrin π-cation radical complexes of **1**−**4** have moderate ferromagnetic interaction between ferryl iron, $S = 1$, and the porphyrin π-radical spin, $S' = {}^1/_2$.

Table 1. ESR Parameters of Oxoiron(IV) Porphyrin π-Cation Radical Complexes

compound	g	E/D	ref
1	3.6, 1.98		*a*
2	3.6, 1.98		*a*
3	3.6, 1.98		*a*
4	3.6, 1.98		*a*
5	4.36, 3.58, 1.99	0.065	*a*
6	4.31, 3.62, 1.99	0.057	*a*
7	4.23, 3.65, 2.00	0.048	*a*
8	4.14, 3.66, 2.00	0.040	*a*
5[b]	4.47, 3.50, 1.98	0.04	20
5[c]		0.067	19
7[b]	4.26, 3.50, 1.98	0.07	20
CAT	3.45, 2		15
ASP	3.27, 1.99		16
HRP	∼2	∼0	12
CPO	2.00, 1.73, 1.64	0.035	14

[a] This work. [b] In dichloromethane−methanol (6:1). [c] Data from Mössbauer spectrum in toluene−methanol.

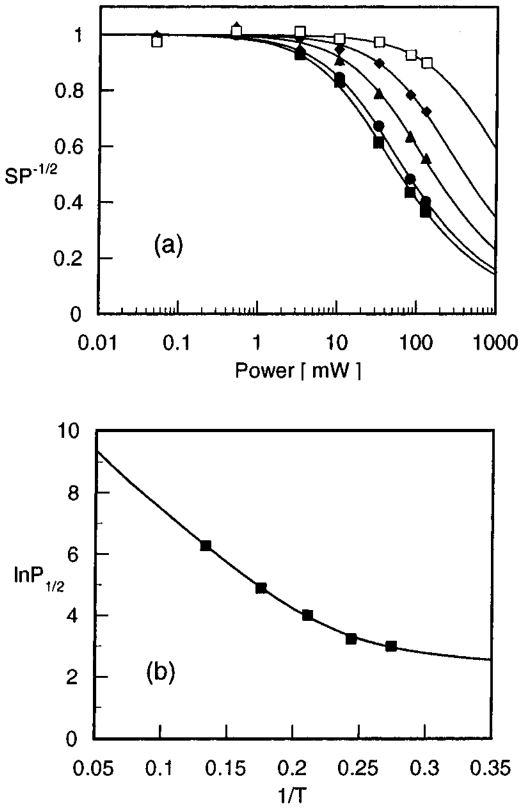

Figure 4. (a) ESR saturation data for **1** as a function of temperature. The signal S is taken as the peak height in the derivative spectrum. The solid lines are fits of $SP^{-1/2} = 1/(1 + P/P_{1/2})^{-1/2}$. Key: ■, 3.7 K; ●, 4.2 K; ▲, 4.8 K; ◆, 5.6 K; □, 7.6 K. (b) Plot of ln $P_{1/2}$ obtained from curve fits of part a vs T^{-1}. The solid line shows the fit based on eq 1.

To further investigate the electronic state, we examined the saturation behavior of the ESR signals of **1**. Because the higher doublets in three Kramers doublets largely determine the spin relaxation rate of the ground doublet, the experiment allows the determination of the energies ΔE_1 and ΔE_2 of the higher doublets. Figure 4a shows ESR saturation data for **1** as a function of temperature. The ESR signal is saturated in the high power microwave region, and the saturation is more effective at low temperature. The data are well fitted by the function of $SP^{-1/2} \propto (1 + P/P_{1/2})^{-1/2}$, where S is the signal intensity, P is the microwave power and $P_{1/2}$ is the half-saturation power. In Figure 4b, we plot the half-saturation power $P_{1/2}$, estimated from a least-squares fit, against $1/T$. On the basis of the model in which the iron(IV) triplet spin couples with the porphyrin π-radical spin, the spin relaxation is

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(25) The g values for **1**−**4** were calculated at peak tops of derivative ESR spectra. Dispersion ESR under rapid-passage conditions for **1** showed $g_\perp \sim 3.1$ and $g_\parallel \sim 2$.

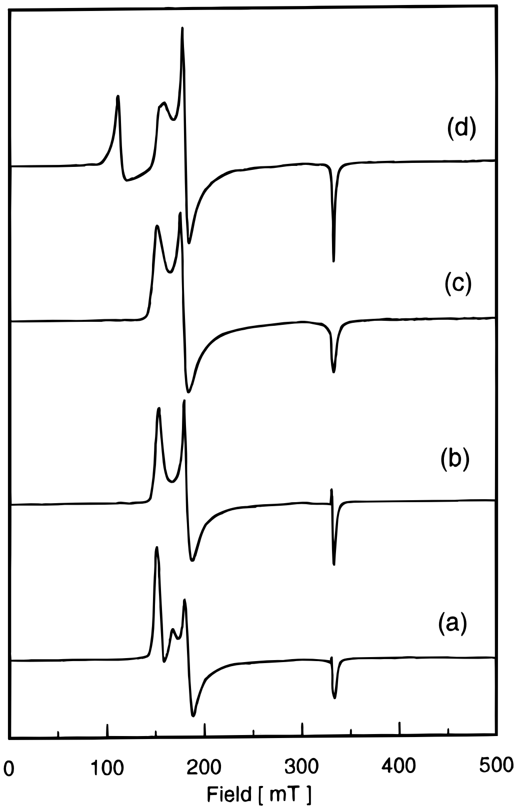

Figure 5. ESR spectra of oxoiron(IV) porphyrin π-cation radicals of **5**−**8** in dichloromethane−methanol (5:1). Conditions: sample concentrations, 1−3 mM; temperature, 14 K, except 20 K for **7**; microwave frequency, 9.30 GHz; microwave power, 0.5−1 mW; time constant, 64 ms; gain, 5 × 10^2 to 2 × 10^3. Key: (a) **5**; (b) **6**; (c) **7**, (d) **8**.

dominated by Orbach processes via excited doublet states, $1/T_1 \propto 1/(\exp(\Delta E/kT) - 1)$ at all but the lowest temperatures. Thus, the data are well fit using the function

$$P_{1/2} = AT + B/[\exp(\Delta E/T) - 1] \qquad (1)$$

with ΔE ~35 K(25 cm^{-1}). Orbach transitions to the highest Kramers doublet are much less efficient than the transition to the intermediate doublet in relaxing the ground doublet; thus, ΔE must be close to the energy ΔE_1 of the latter. The estimated ΔE value was close to the D value of HRP compound I and much smaller than that of CPO compound I.

ESR Spectra of $\mathbf{A_{2u}}$ Radical Complexes. To compare the ESR spectral features between the a_{1u} and the a_{2u} radical complexes, we measured the ESR spectra of the oxoiron(IV) porphyrin π-cation radical complexes of **5**−**8**. In a previous paper, we have reported that the oxoiron(IV) porphyrin π-cation radical complex of **5** has an a_{2u} radical state and the a_{2u} state gradually shifts to the a_{1u} state with an increase in electronegativity of the meso substituent; with going from **5** to **8**.[21] Figure 5 shows the ESR spectra of the oxoiron(IV) porphyrin π-cation radical complexes of **5**−**8** in dichloromethane−methanol (5:1) at 14 K. The g values are summarized in Table 1. For all four complexes, we observed typical $S = {}^3/_2$ ESR spectra that have effective g values $g_y \sim 4.3$, $g_x \sim 3.7$, and $g_z \sim 1.99$. Interestingly, with an increase in electronegativity of the *meso*-substituent, the g_y signal decreases its intensity relative to the g_x signal. Furthermore, the separation between the g_x and g_y signals is decreased with an increase in electronegativity of the *meso*-substituent. Because the separation between g_x and g_y signals is proportional to the E/D value in the first-order perturbation, the decrease indicates a decrease in the E/D value.

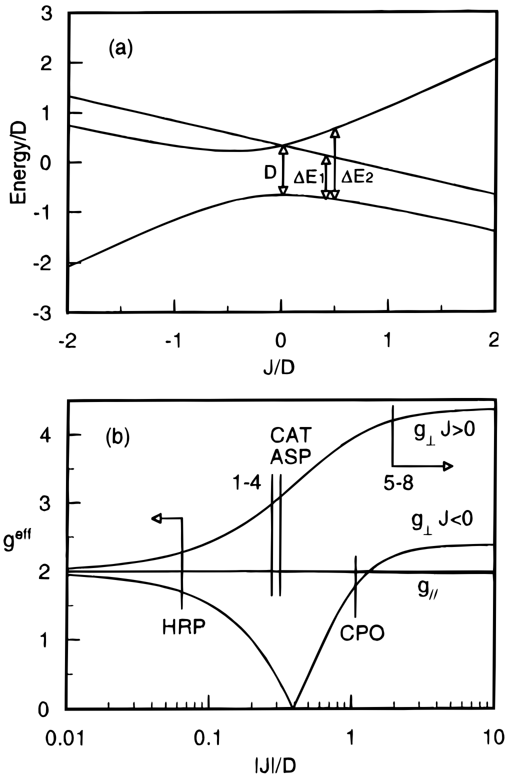

Figure 6. (a) Energies of Kramers doublets formed from eq 1 in units of the zero-field parameter D as a function of J/D. (b) The effective g values, $g_\perp^{\mathrm{eff}}$ and $g_\parallel^{\mathrm{eff}}$, obtained from eq 2, as a function of $|J|/D$ for the lowest Kramers doublet. The ferryl g values are taken to be $g_\perp = 2.23$ and $g_\parallel = 1.96$, which are appropriate for the case $D \sim 30$ K,[31] and an isotropic g value of 2.0 is used for the porphyrin π-cation radical.

From ESR analysis based on an $S = {}^3/_2$ spin Hamiltonian,[18] we estimated the E/D values for **5**−**8** and summarized them in Table 1. As expected from the ESR spectra, the E/D value decreases with an increase of electronegativity of the *meso*-substituent.

Discussion

A variety of ESR spectra for the oxoiron(IV) porphyrin π-cation radical species have been reported; nevertheless, all can be analyzed in terms of a spin coupling, as described by eq 2, between the zero-field split ferryl iron (S = 1) and the

$$H' = -J\mathbf{S}\cdot\mathbf{S}' + D(\mathbf{S}_z^{\,2} - {}^2/_3) + E(\mathbf{S}_x^{\,2} - \mathbf{S}_y^{\,2}) \qquad (2)$$

porphyrin π-cation radical (S′ = 1/2), where J is the spin coupling parameter and D and E are the zero-field splitting parameters of ferryl iron. By operating six eigenfunctions in eq 2, three Kramers doublets which remain 2-fold degenerate in zero field are formed. For axial symmetry ($E = 0$) and isotropic J, the eigenfunctions depend on the ratio J/D only. Figure 6a shows the change in energies of the three Kramers doublets against J/D.

As shown in Figure 6a, the lowest Kramers doublet is well separated in energy from the two higher ones. Thus, the observed ESR signals for the oxoiron(IV) porphyrin π-cation radicals arise from the ESR transitions in the lowest Kramers doublet. Operating the eigenfunctions for the lowest Kramers doublets in eq 3, we estimated the change in g values relative

$$H = H' + \mathbf{g}\beta\mathbf{H}\cdot\mathbf{S} + g'\beta\mathbf{H}\cdot\mathbf{S}' \qquad (3)$$

J/D, where **H** is the applied magnetic field and **g** and g' are g values for ferryl iron and the porphyrin π-cation radical, respectively. Figure 6b shows the change in effective g values,

g^{eff}, for isotropic J and $E = 0$ as a function of $|J|/D$. The effective g value along the heme normal ($g_{\|}{}^{\mathrm{eff}}$) is essentially constant for all values of J/D. The effective g value along the heme plane ($g_{\perp}{}^{\mathrm{eff}}$) increases monotonically with J/D for ferromagnetic coupling while the $g_{\perp}{}^{\mathrm{eff}}$ value passes through zero at $J/D \sim 0.4$ for antiferromagnetic coupling.

The present ESR spectra of the oxoiron(IV) porphyrin π-cation radicals of **1**−**8** are well interpreted by Figure 6. The ESR spectra of the a_{1u} radical complexes, **1**−**4**, which give $g_{\perp}{}^{\mathrm{eff}} \sim 3.1$ and $g_{\|}{}^{\mathrm{eff}} \sim 2.0$, represent ferromagnetic coupling with an intermediate strength of $|J|/D \sim 0.3$ while the a_{2u} radical complexes, **5**−**8**, show strong ferromagnetic coupling, $|J|/D > \sim 1$. Giving $|J|/D = 0.3$ for the a_{1u} oxoiron(IV) porphyrin π-cation radical complexes, we can calculate the energies of the excited Kramers doublets to be $\Delta E_1/D = 0.88$ and $\Delta E_2/D = 1.23$, as shown in Figure 6a. If we identify the energy of the lower level, ΔE_1, with ΔE, $\Delta E = \sim 25$ cm^{-1} as found by fitting the spin relaxation data, we find $D = \sim 28$ cm^{-1} for the ferryl iron state. The obtained D value is larger than that of **5**: 18.6 cm^{-1} by Boso et al.[19] and 25 cm^{-1} by Mandon et al.[20] We also calculated the isotropic J value, $J \sim +8$ cm^{-1}, from the present D and $|J|/D$ values. The obtained J value clarifies the moderate ferromagnetic coupling for **1** and the value is much smaller than that of **5** whose J value is more than $+43$ cm^{-1}.[19,20]

The finding of ferromagnetic interaction for both a_{1u} and a_{2u} complexes is reasonable for an oxoiron(IV) porphyrin π-cation radical state. As emphasized by Reed et al.,[26] a net overlap between the d_{xz} and d_{yz} orbitals of ferryl iron and the π-orbital of the porphyrin ring would not be allowed even though the symmetry of the porphyrin ring is reduced from 4- to 2-fold symmetry; therefore, a ferromagnetic coupling is expected for both a_{1u} and a_{2u} radical complexes. To be an antiferromagnetic coupling like the CPO compound I, the distortion must include a further lowering in symmetry, for example, a buckling of the ring.

It is worth noting that the spin coupling in the a_{2u} complex is larger than that in the a_{1u} complex. This is explained by the spin densities at the pyrrole nitrogen atom in the a_{1u} and a_{2u} orbitals.[27,28] In the a_{2u} orbital, a large spin density exists on the pyrrole nitrogen atom, which leads to a strong ferromagnetic interaction if metal and porphyrin orbitals are orthogonal. On the other hand, a magnetic interaction for the a_{1u} orbital would be weak because the pyrrole nitrogen atom is a node. Furthermore, we should take account of the fact that the porphyrin plane of **1** is much more flexible than that of **5**. We have reported that the copper(II) porphyrin π-cation radical of **1** has weak antiferromagnetic coupling.[28] On the other hand, Erler et al. showed a strictly planar structure and a strong ferromagnetic interaction for the copper(II) porphyrin π-cation radical of **5**.[29] Since a ferromagnetic interaction would be expected for both complexes if porphyrin is strictly planar, the weak antiferromagnetic coupling observed for **1** suggests some deviation from D_{4h} symmetry in its geometry. Actually, the observed D value for copper(II) porphyrin π-cation radical of **1** was much larger than that of **5**. This is also the case for the oxoiron(IV) porphyrin π-cation radical complex. Considering the present large D value for **1**, we expected some distortion of the porphyrin plane of **1**, which results in a decrease of the J value. Asymmetric substitution at the pyrrole β position(methyl and aryl groups) and no substituent at the *meso*-position make the porphyrin plane flexible. The small $|J|/D$ values for **1**−**4**, compared with those of **5**−**8**, may reflect on these points, together with the orbital symmetry(spin density) of the radical orbital.

Table 2. Spin Hamiltonian Parameters of Oxoiron(IV) Porphyrin π-Cation Radical Complexes and Compound I

compound	J/D	D (cm^{-1})	J[a]	E/D	ref
1 (a_{1u} complex)	0.3	28	+8		[b]
5 (a_{2u} complex)	1.7[c]	25	+43	0.04	20
		18.6	$J \geq D$	0.067	19
7 (a_{2u} complex)	1.5[c]	25	+38	0.07	20
CAT	0.4				15
ASP	0.28(0.4[d])				16
HRP	≤±0.1	26	≤±2.6[e]	~0	12
CPO	−1.02	37	−38[e]	0.035	14

[a] Exchange interaction was defined by eq 2. Thus, a positive J value means ferromagnetic interaction and a negative J is antiferromagnetic interaction. [b] This work. [c] The value was calculated from D and J values. [d] From Figure 6b. [e] The value was obtained from J/D and D values.

On the basis of the present ESR results, we would like to discuss the electronic state of compound I. The present ESR spectra of the a_{1u} oxoiron(IV) porphyrin π-cation radical complexes (**1**−**4**) resemble those of compound I of CAT and ASP. Further, as summarized in Table 2, the detailed ESR analysis showed that the $|J|/D$ values for compound I of CAT ($|J|/D = 0.4$) and compound I of ASP ($|J|/D = 0.28$) are similar to those of the a_{1u} radical complexes but not similar to those of the a_{2u} complex. Although the axial ligand in the present model complexes is different from that in CAT and ASP, these similalities allow us to expect the a_{1u} radical states for compound I of CAT and ASP. The a_{1u} radical state is also quite reasonable from previous resonance Raman[30] and NMR[21] studies where the a_{1u} state is predominant for the iron protoporphyrin (meso-unsubstituted porphyrin) π-cation radical complex.

As shown in Figure 6b and Table 2, a variety of |J|/D values have been reported for compound I in heme enzymes while those for model complexes are uniform. This may be explained by the idea discussed by Benecky et al.,[15] where the nature of the proximal ligand relates to the sign and magnitude of the exchange parameter (J) and the zero-field parameter (D). The sixth ligand of the present model complexes is methanol while various axial ligands have been known in heme enzymes; phenolate from tyrosine in CAT, imidazole from histidine in HRP and ASP, and thiolate from cystein in CPO. Weak coordinations of methanol and phenolate in CAT, and imidazole in ASP to ferryl iron would maintain the orbital orthogonality, which leads to ferromagnetic interaction. In contrast, the effective symmetry of compound I in CPO and HRP is lowered by axial thiolate and imidazole ligands. The strong π-bonding character of thiolate in CPO increases the orbital overlap to the point that antiferromagnetic coupling dominates while HRP represents a presumably fortuitous balance where $J \sim 0$.

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