length, and the large mixing and conformational entropy in the interlayer space. The large mixing entropy impedes demixing of the surfactant anions to form films of different thicknesses.

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Contribution from the Department of Chemistry, Faculty of Science, and Division
of Molecular Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Spin Coupling in Ferric Porphyrin and Chlorin π-Cation-Radical Complexes

Satoru Nakashima,[1] Hiroaki Ohya-Nishiguchi,*,[1] Noboru Hirota,[1] Hiroshi Fujii,[2] and Isao Morishima*,[2]

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The ferric porphyrin π-cation-radical complexes (OEP$^\bullet$)Fe^{III}(ClO$_4$)$_2$ (**1**) (OEP$^\bullet$ = monoanion of octaethylporphyrin) and (OEP$^\bullet$)Fe^{III}Cl[SbCl$_6$] (**2**) and the ferric chlorin π-cation-radical complexes (OEC$^\bullet$)Fe^{III}(ClO$_4$)$_2$ (**3**) (OEC$^\bullet$ = monoanion of octaethylchlorin), (OEC$^\bullet$)Fe^{III}Cl[SbCl$_6$] (**4**), and (TPC$^\bullet$)Fe^{III}Cl[SbCl$_6$] (**5**) (TPC$^\bullet$ = monoanion of tetraphenylchlorin) were examined in microcrystalline form by magnetic susceptometry over a range of 1.6 K to room temperature at an applied field. The effective magnetic moments of the two six-coordinate complexes, **1** and **3**, were in reasonable agreement with simulation in which an $S = {}^5/_2$ iron ion antiferromagnetically couples with an $s = {}^1/_2$ porphyrin (or chlorin) π radical by weak exchange interaction. In the five-coordinate complexes, **2**, **4**, and **5**, the results of the magnetic susceptibility measurements are consistent with the calculations based on the model that the $S = {}^5/_2$ iron ion antiferromagnetically couples with the $s = {}^1/_2$ π radical with energies of -8 cm^{-1} for **2**, -20 cm^{-1} for **4**, and -85 cm^{-1} for **5**. Thus the ground states of all these complexes measured are of total spin $S_T = 2$. The difference in the magnitude of the antiferromagnetic coupling between the five-coordinate complexes and the six-coordinate complexes is reasonably explained by the difference of the symmetry of the radical orbitals: A$_{1u}$ symmetry of OEP, OEC, and TPC complexes. From these results A$_{1u}$ symmetry for the radical orbitals in horseradish peroxidase compound I (HRP compound I) and myeloperoxidase compound I (MPO compound I) is proposed.

Introduction

In recent years a number of heme and non-heme enzymes that exhibit intramolecular spin-coupling phenomena have been explored.[3-5] For example, it has been suggested that in HRP (horseradish peroxidase) compound I, the $S = 1$ spin of the central Fe(IV) ion weakly couples antiferromagnetically with an $s = {}^1/_2$ porphyrin π-cation-radical spin to produce a spin system with an overall $S = {}^1/_2$.[6-10] These states in the native enzymes have received continuous interest, since they might be closely related to chemical and biological functions.

Since the success of chemical oxidation of synthesized iron(III) porphyrin complexes,[11-15] various oxidative states of metalloporphyrins have been examined as model complexes for these heme enzymes.[16-23] So it has become increasingly important to recognize the coupling behavior between the central iron ion and the ligand π radical, whether the coupling mode is ferromagnetic, antiferromagnetic, or virtually absent. Furthermore, when each of these three situations is known, a qualitative understanding of the circumstances under which each will occur becomes the next problem.

Gans et al.[24] have proposed a theory to account for the notable difference in coupling of the metal ion and the ligand spin between (TPP$^\bullet$)Fe^{III}(ClO$_4$)$_2$ and (TPP$^\bullet$)Fe^{III}Cl[SbCl$_6$] (TPP$^\bullet$ = monoanion of tetraphenylporphyrin). Spin coupling in the former compound is ferromagnetic, while that in the latter is antiferromagnetic. Their theory is based on the occupations and symmetries of a radical orbital that is related to magnetic coupling. They have reported that in the TPP system the π radical orbital has A$_{2u}$ symmetry, which leads to ferromagnetic coupling in D_{4h} symmetry and to antiferromagnetic coupling in lower C_{2v} symmetry.

In this paper we wish to report the magnetic properties of spin coupling in Fe(III) complexes with OEP, OEC, and TPC π cation

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(2) Division of Molecular Engineering.

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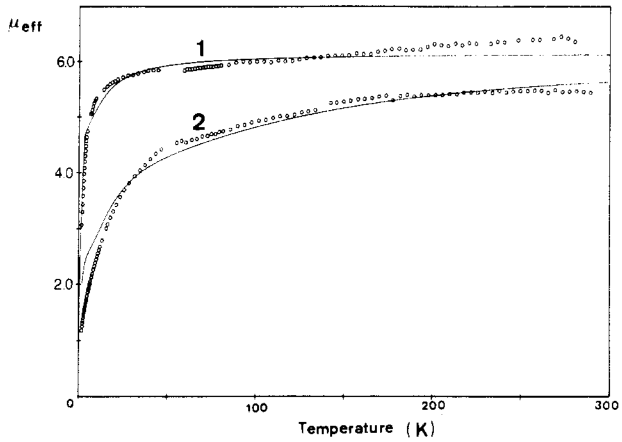

Figure 1. Temperature dependence of μ_{eff} for $(OEP^{\bullet})Fe(ClO_4)_2$ (**1**) and $(OEP^{\bullet})FeCl[SbCl_6]$ (**2**).

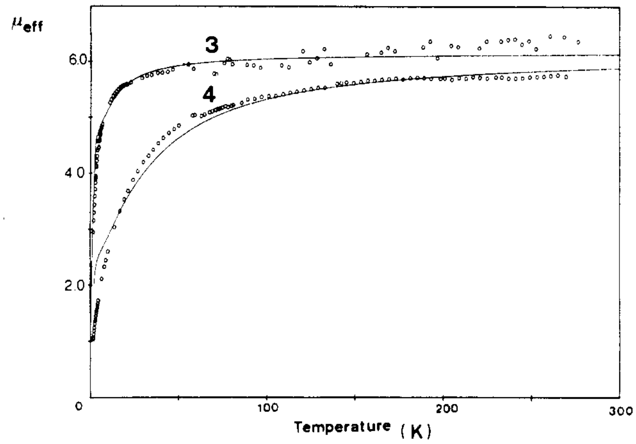

Figure 2. Temperature dependence of μ_{eff} for $(OEC^{\bullet})Fe(ClO_4)_2$ (**3**) and $(OEC^{\bullet})FeCl[SbCl_6]$ (**4**).

radicals, $(OEP^{\bullet})Fe^{III}(ClO_4)_2$ (**1**), $(OEP^{\bullet})Fe^{III}Cl[SbCl_6]$ (**2**), $(OEC^{\bullet})Fe^{III}(ClO_4)_2$ (**3**), $(OEC^{\bullet})Fe^{III}Cl[SbCl_6]$ (**4**), and $(TPC^{\bullet})Fe^{III}Cl[SbCl_6]$ (**5**). Differing from the case of the TPP system, the interaction in the six-coordinate complexes (**1** and **3**) is virtually absent. The five-coordinate complexes (**2**, **4**, and **5**) show antiferromagnetic interaction. A structural explanation proposed by Gans et al.[24] will be used to show how the difference from the TPP system arises and how the difference between the five-coordinate and the six-coordinate complexes emerges. From these considerations **1**–**5** are well explained to have another kind of symmetry, A_{1u}, compared with that of the TPP systems. Our result that these complexes have A_{1u} symmetry is consistent with the results obtained from other spectroscopic techniques.

These complexes are expected to be models of HRP compound I (OEP system) and MPO compound I (OEC system).[25,26] First, it is because these enzymes have porphyrin or chlorin with the iron ion in their active site. Second, our results of spin coupling in the six-coordinate complexes resemble those of HRP compound I and MPO compound I, in which the presence of weak antiferromagnetic coupling has been suggested. We discuss their spin states on the basis of the present results. Our results will give a new insight into the question about the spin coupling in the native enzymes.

Experimental Section

Measurements. Magnetic susceptibility measurements were carried out by using a microcomputer-controlled magnetic torsion balance and the Faraday method to measure the susceptibility from 1.6 K to room temperature. Microcrystalline powder samples of 30–50 mg were used. The temperatures of samples were measured by a Au(Co)–Cu thermocouple and a Ge resistor, which were calibrated against the magnetic susceptibility of the Mn Tutton salt.[27] The applied field gradient was estimated from the susceptibility of $HgCo(SCN)_4$.[28] ESR measurements were performed by a JEOL Fe-3X X-band spectrometer. Temperatures as low as 4.2 K were attained by using an Air Products Model LTR-3-110 cryostat. The CNDO/2 MO calculations were carried out at the Computer Center of Kyoto University.

Material. (Octaethylporphyrinato)iron(III) chloride, $(OEP)Fe^{III}Cl$,[29] and (octaethylchlorinato)iron(III) chloride, $(OEC)Fe^{III}Cl$,[29,30] were prepared by literature methods. Tetraphenylchlorin was synthesized by the published method,[29] and iron was incorporated by the standard acetic acid reflux method.[29] $(OEP^{\bullet})Fe^{III}(ClO_4)_2$ (**1**) and $(OEC^{\bullet})Fe^{III}(ClO_4)_2$ (**3**) were prepared from $(OEP)Fe^{III}Cl$ and $(OEC)Fe^{III}Cl$ by using silver perchlorate as oxidant.[31] $(OEP^{\bullet})Fe^{III}Cl[SbCl_6]$ (**2**), $(OEC^{\bullet})Fe^{III}Cl[SbCl_6]$ (**4**), and $(TPC^{\bullet})Fe^{III}Cl[SbCl_6]$ (**5**) were synthesized from $(OEP)Fe^{III}Cl$, $(OEC)Fe^{III}Cl$, and $(TPC)Fe^{III}Cl$ by using phenoxathiin hexachloroantimonate as oxidant.[32] From UV and IR spectra, these complexes were identified as ferric π cation radicals rather than Fe(IV) complexes as previously reported.[24,32]

Results

The effective magnetic moment (μ_{eff}) is more convenient than the magnetic susceptibility (χ) itself for investigating the spin states of the complex compounds. Therefore, μ_{eff} values of the complexes were derived from the measured values of χ by $\mu_{eff}{}^2 = 3kT\chi/\mu_B{}^2$. However, when the magnetic properties of the complex are discussed, it is useful to show χ, instead of μ_{eff}. χ will be shown when necessary.

Effective Magnetic Moments of $(OEP^{\bullet})Fe^{III}(ClO_4)_2$ (1) and $(OEP^{\bullet})Fe^{III}Cl[SbCl_6]$ (2). The μ_{eff} values of **1** and **2** are plotted as functions of temperature in Figure 1. The upper dots show μ_{eff} values of **1**, and the lower show those of **2**. The μ_{eff} of **1** increases with temperature, approaching 6.0–6.2 μ_B (Bohr magneton) at high temperatures. When there is no coupling between the iron ($S = {}^5/_2$) and the π-radical spins ($s = {}^1/_2$), that is, when the two spins behave independently, μ_{eff} should be 6.1 μ_B. Therefore, high-temperature values of **1** indicate clearly that the interaction between the two spins is very small in **1**, so that these two spins behave independently. The behavior of μ_{eff} in the low-temperature region, where it drops suddenly, shows that this complex has a zero-field splitting (D) smaller than 1 cm^{-1}.

The μ_{eff} of **2** gradually increases as the temperature rises, approaching 5.3 μ_B at room temperature. If there is strong antiferromagnetic coupling between the iron and the π-radical spins, the ground state of this complex becomes $S = 2$, which leads to $\mu_{eff} = 4.9$ μ_B. On the contrary, if the coupling is ferromagnetic, the ground state is $S = 3$, where μ_{eff} exhibits 6.9 μ_B. The experimental results indicate that antiferromagnetic coupling larger than that in **1** exists between the iron and the π-radical spins. Since this antiferromagnetic coupling is relatively small compared with the thermal energy at room temperature, the excited state ($S = 3$) is also thermally occupied as the temperature rises. In this case the μ_{eff} increases more than 4.9 μ_B as the temperature approaches room temperature.

Effective Magnetic Moments of $(OEP^{\bullet})Fe^{III}(ClO_4)_2$ (3) and $(OEC^{\bullet})Fe^{III}Cl[SbCl_6]$ (4). The measured values of the μ_{eff} of **3** and **4** are plotted as functions of temperature in Figure 2. The upper dots show μ_{eff} values of **3**, and the lower show those of **4**. A tendency similar to that in the OEP system can be seen in these two complexes. The μ_{eff} of **3** increases toward 6.0–6.3 μ_B and abruptly drops with lowering of the temperature. The μ_{eff} of **4** gradually increases toward 5.7 μ_B. The only difference between the OEP and OEC systems is in the μ_{eff} values of **2** and **4** at high temperatures: 5.7 μ_B for **4** is larger than the value for **2** because

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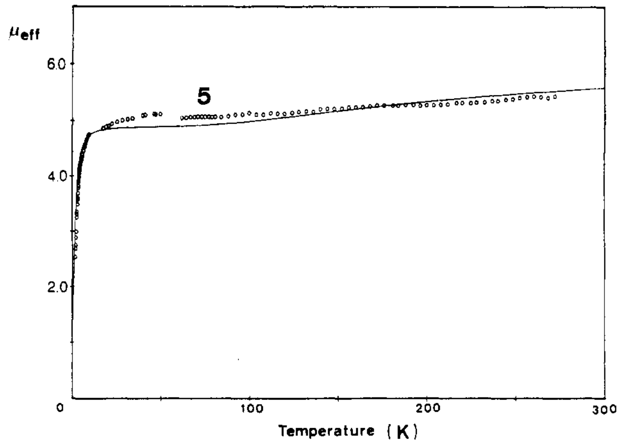

Figure 3. Temperature dependence of μ_{eff} for (TPC•)FeCl[SbCl$_6$] (5).

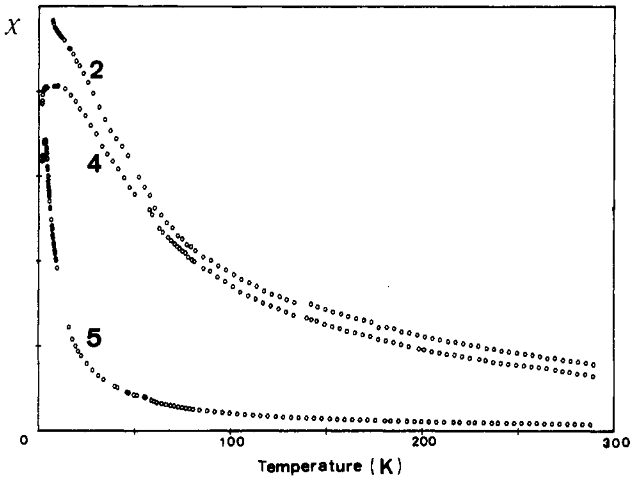

Figure 4. Temperature dependence of χ for **2**, **4**, and **5**. The magnitude of the longitudal axis is changed in each complex, for comparison.

the magnitude of the antiferromagnetic coupling is smaller in it than in **2**.

Effective Magnetic Moment of (TPC•)Fe^{III}Cl[SbCl$_6$] (5). The measured values of the μ_{eff} of **5** are plotted as a function of temperature in Figure 3. The μ_{eff} of **5** gradually increases as the temperature rises, approaching 5.2 μ_B at high temperatures. This result suggests a comparatively large antiferromagnetic coupling between the iron and the π-radical spins.

Magnetic Susceptibility of the Five-Coordinate Complexes, 2, 4, and 5. The observed values of the magnetic susceptibility (χ) of the five-coordinate complexes (**2**, **4**, and **5**) are plotted in Figure 4. In the extremely low temperature region, χ deviates from the Curie law, dropping to zero, especially in the case of **4**. Since the iron–radical coupled spin in each heme unit interacts with one another antiferromagnetically, the magnetic susceptibility decreases toward zero in the low-temperature region. χ of **2** does not drop completely and gives a shoulder around 10 K. This may be due to the fact that **2** is difficult to recrystallize so that monomeric impurities remained in the system and raised the susceptibility.

ESR Measurements. ESR spectra of the complexes (**1**–**5**) were recorded both on powder samples and in CH$_2$Cl$_2$ solutions at 4.2 K. No signal could be detected except for a very small amount of impurities. As the iron spin ($S = {}^5/_2$) is coupled to the radical spin, the total spin state becomes an integer, where the X-band ESR signal cannot be detected in the usual magnetic field.

Analysis

In order to explain the experimental results of the six-coordinate complexes, **1** and **3**, the following Hamiltonian can be used

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) - J\mathbf{S}\cdot\mathbf{s} + g\mu\mathbf{H}(\mathbf{S} + \mathbf{s}) \qquad (1)$$

where **S** is the spin with $^5/_2$ on the iron ion, **s** is the spin with $^1/_2$ on the porphyrin or on chlorin ligand, and D and E are the zero-field-splitting parameters of the iron ion. In our cases E can be neglected because of the axial symmetry of the complexes. J is the exchange interaction (spin coupling) between the iron spin and the π-radical spin. The last term in eq 1 is the Zeeman-splitting term, which is induced in an external magnetic field.

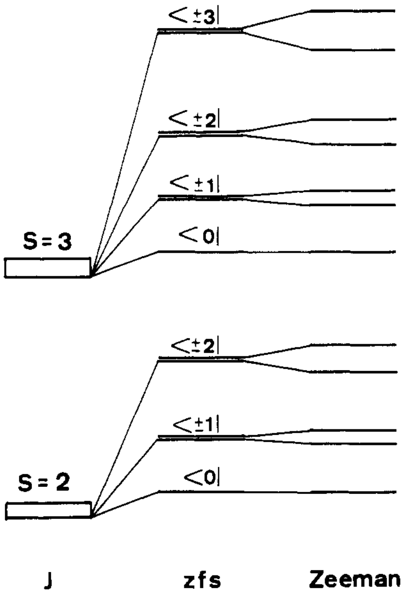

Figure 5. Energy states derived from the Hamiltonian (1) and the eigenfunctions (2) in the case of antiferromagnetic coupling with a field applied to the z direction.

Table I. Hamiltonian Parameters Used To Fit the Experimental Results

compd	J, cm^{-1}	D, cm^{-1}	J', cm^{-1}
(TPP•)Fe(ClO$_4$)$_2$[a]	110	12	
(TPP•)FeCl[SbCl$_6$][a]	−200	3	−0.65
(TPC•)FeCl[SbCl$_6$] (**5**)	−85 ± 5		−0.5 ± 0.2
(OEP•)Fe(ClO$_4$)$_2$ (**1**)	−5.5 ± 1	0.7 ± 0.1	
(OEP•)FeCl[SbCl$_6$] (**2**)	−20 ± 2	5.5 ± 1	−1.4 ± 0.5
(OEC•)Fe(ClO$_4$)$_2$ (**3**)	−5.5 ± 1	0.7 ± 0.1	
(OEC•)FeCl[SbCl$_6$] (**4**)	−8 ± 1	5.5 ± 1	−1.0 ± 0.5

[a] Reference 33.

To obtain the eigenfunction of total spin, we use the eigenfunction of $S = {}^5/_2$ and $s = {}^1/_2$ with the Wigner coefficient

$$|S_T M_s\rangle = \sum_{M,m} \langle {}^5\!/_2 M\ {}^1\!/_2 m\rangle |{}^5\!/_2 M\rangle |{}^1\!/_2 m\rangle \qquad (2)$$

where S_T means total spin and M_s is its magnetic quantum number. From these eigenfunctions we can obtain the eigenvalues of the state, which are illustrated in Figure 5 in the case of antiferromagnetic coupling ($J < 0$) with a field applied to the z direction. Assuming Boltzmann distribution of M_S in these states, the magnetic susceptibility, χ_{mol}, becomes

$$\chi_{mol} = N_A \frac{\sum_i \frac{M_{s,i}g}{H} \exp\left(-\frac{E_i}{kT}\right)}{\sum_i \exp\left(-\frac{E_i}{kT}\right)} \qquad (3)$$

where E_i represents energy levels derived from diagonalizing the matrix elements of the Hamiltonian (1) and $M_{s,i}$ is a magnetic quantum number of ith state.

The μ_{eff} of each complex is also calculated. These theoretical values at various temperatures were calculated by using a microcomputer to fit the theoretical curve to the experimental data. The values of exchange interaction (J) and zero-field splitting (D) were determined so as to fit the overall temperature dependence of the observed values. The obtained values are listed in Table I. J and D are actually independent of each other, so that we

Table II. Symmetries of d Orbitals under D_{4h} and C_{2v} Symmetries

	D_{4h}	C_{2v}
$d_{x^2-y^2}$	b_{1g}	a_1
d_{z^2}	a_{1g}	a_1
d_{xz}	e_g	b_1
d_{yz}	e_g	b_2
d_{xy}	b_{2g}	a_2
radical	A_{1u}	A_2
	A_{2u}	A_1

can determine J and D by fitting the curve in the high-temperature region and in the low-temperature region, respectively. The theoretical curves for **1** and **3** calculated with the values in Table I are drawn in Figures 1 and 2, respectively. It is shown that the agreement between the experimental data and the calculated curves is extremely good.

In the six-coordinate complexes, **1** and **3**, the exchange interactions between the $S = {}^5/_2$ iron ion and the $s = {}^1/_2$ π radical are very weak and antiferromagnetic. Then two spins behave independently at high temperatures. This is quite different from the results of the TPP system.[24] Lang et al.[33] reported that $(\text{TPP}^\bullet)\text{Fe}^{\text{III}}(\text{ClO}_4)_2$ has a ferromagnetic coupling of 110 cm^{-1}.

As is often the case for five-coordinate heme complexes, there also exists spin coupling between heme units which are arranged in face-to-face pairs.[33-36] This coupling influences magnetic susceptibility in the extremely low temperature region where it drops toward zero. To interpret this behavior of χ, we introduce an inter-heme coupling, J', by considering the following Hamiltonian

$$\mathcal{H} = \mathcal{H}_{1(1)} + \mathcal{H}_{2(1)} - J'\mathbf{S}_1\cdot\mathbf{S}_2 \qquad (4)$$

where the first two terms mean the Hamiltonian used in eq 1 for each heme of a pair and the last term is the inter-heme coupling that we are considering now. Here also, $\mathbf{S}_1$ and $\mathbf{S}_2$ are total spins which are composed of the $S = {}^5/_2$ iron ion and the $s = {}^1/_2$ π radical.

In this case a simulation similar to the case of the six-coordinate complexes had been done. The calculated values of μ_{eff} of each complex were fitted to the experimental data to estimate their J, D, and J' values. The values obtained from this simulation are also listed in Table I, and the calculated curves are drawn in Figures 1 and 2. In **2** and **4**, the coupling J is antiferromagnetic with magnitudes of -20 and -8 cm^{-1}, which are relatively smaller than those in the case of $(\text{TPP}^\bullet)\text{Fe}^{\text{III}}\text{Cl}[\text{SbCl}_6]$ reported by Lang et al.[33] They reported that the magnitude of this antiferromagnetic coupling is -200 cm^{-1}1. Our results in the case of OEP and OEC systems are one-tenth smaller than that of the TPP system.

Discussion

The following discussion is based on the theory that Gans et al.[24] used to explain the results of the TPP system. The explanation for the different magnitudes of the coupling was based on the different symmetries of their structures, especially coordination environments.[36b]

First, the six-coordinate complexes, **1** and **3**, are more symmetrical than the five-coordinate ones. The structure of the six-coordinate complexes consists of a planar porphyrin or chlorin, two axial ligands, and the iron atom located at the center of symmetry. In such a circumstance, the iron atom is effectively put in the ligand field with D_{4h} symmetry. In this point group each d orbital of the iron ion, which is occupied by one electron, has proper symmetry such as b_{1g} of $d_{x^2-y^2}$ etc. Each corresponding symmetry is listed in Table II.

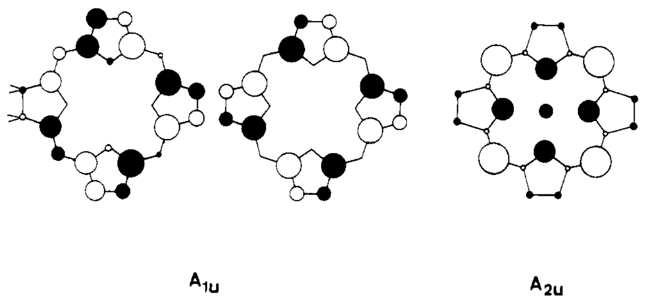

Figure 6. Results of the CNDO/2 MO calculation under A_{1u} and A_{2u} symmetries.

Second, the same argument can be used in the case of the five-coordinate complexes, **2**, **4**, and **5**. The structure of the five-coordinate complexes consists of a saddle-shaped porphyrin or chlorin, one unsymmetrical axial ligand, and one iron atom deviating from the plane. Then the iron atom can be regarded as being located in a site with C_{2v} symmetry. The symmetries of d orbitals in C_{2v} symmetry are also deduced and are listed in Table II.

Next, the spin densities of the half-filled orbitals of porphyrin and chlorin have been derived by CNDO/2 MO calculations. The calculated spin densities under the symmetries of A_{1u} and A_{2u} are shown in Figure 6. The difference between an orbital of A_{2u} symmetry and an orbital of A_{1u} symmetry is in the spin densities on nitrogens around the iron atoms, as is shown in Figure 6. In A_{2u} symmetry the orbital spin densities on the nitrogens are so large that the radical orbital is strongly affected by Hund's rule. On the other hand, in A_{1u} orbital symmetry the spin densities on the nitrogens are very small so that the interaction should be very small.

We now discuss the exchange coupling in these symmetries, such as D_{4h} for six-coordinate and C_{2v} for five-coordinate complexes.

(i) 1 and 3 with D_{4h} Symmetry. The six-coordinate complexes of **1** and **3** are considered to have D_{4h} symmetry. In this symmetry the π radical has A_{1u} or A_{2u} symmetry. According to the results of Gans et al., the π-radical orbital of TPP is in A_{2u} symmetry, so that this orbital has a symmetry different from that of all of the d orbitals. This means that these six orbitals, the π-radical orbital and the d orbitals, are strictly orthogonal to each other. So the $S_T = 3$ ground state of maximum multiplicity can be derived according to Hund's rule, which leads to large ferromagnetic coupling as in the case of the $(\text{TPP}^\bullet)\text{Fe}$ system.

The OEP and OEC systems, on the contrary, are considered to have radical orbitals of A_{1u} symmetry.[21c,37,38] If they had A_{2u} symmetry, the results should be the same as in the case of TPP, ferromagnetic coupling. However, the μ_{eff} values of **1** and **3** obtained experimentally show antiferromagnetic coupling on the order of -5 cm^{-1}. Therefore these results of the OEP and OEC systems cannot be explained by the assumption of having A_{2u} symmetry. The radical orbital of A_{1u} symmetry does not have the same symmetry as all the d orbitals either. As was shown in Figure 6, the spin densities on the nitrogens in the A_{1u} orbital are very small so that the coupling should be very small, which makes the spin on the radical orbital behave independently. Practically, these six-coordinate complexes do not have ideal D_{4h} symmetry, so the radical orbital mixes slightly with the d orbitals and the coupling becomes weakly antiferromagnetic. This consideration that OEP and OEC have the radical orbital of A_{1u} symmetry is consistent with the experimental results.

(ii) 2 and 4 with C_{2v} Symmetry. This is the case of five-coordinate complexes. In this symmetry the A_{1u} and A_{2u} symmetries mentioned above are reduced to A_2 and A_1, respectively. And the symmetry of each d orbital is also reduced, as shown in Table

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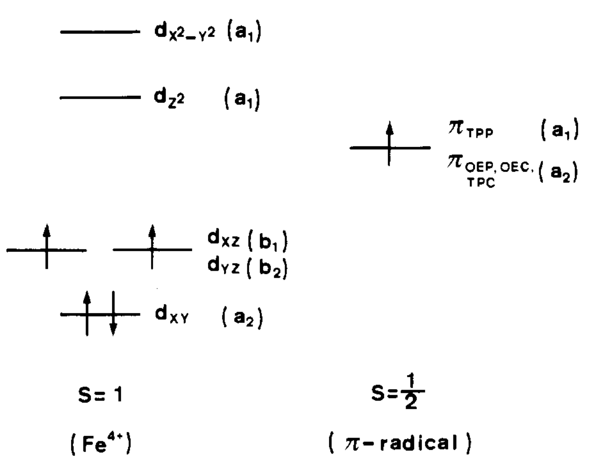

Figure 7. Symmetries of d orbitals and π orbitals under C_{2v} symmetry.

II. The A_1 radical orbital of TPP has the same symmetry as $d_{x^2-y^2}$ and d_{z^2}. Under such lower symmetry the overlap of the radical orbital with two metal orbitals becomes symmetrically allowed. This causes antiferromagnetic coupling, giving a resultant $S = 2$ ground state. The same description can be used for the OEP and OEC systems. However, the radical orbital of A_2 symmetry in these systems has a smaller amount of spin density on the nitrogens as compared with the case of TPP, so that the magnitude of the coupling becomes smaller than that of the TPP system. Thus it is consistent with the experimental results that antiferromagnetic coupling of OEP (−20 cm^{-1}), OEC (−8 cm^{-1}), and TPC (−85 cm^{-1}) is smaller than that of TPP (−200 cm^{-1}).

Application to the Symmetry of HRP Compound I and MPO Compound I. We now discuss the symmetries of the radical orbitals of HRP compound I and MPO compound I. The magnetic properties of the six-coordinate OEP and OEC systems described above resemble those of HRP compound I or MPO compound I. It is suggested that the iron(IV) $S = 1$ spin weakly couples with the π radical antiferromagnetically.

Assuming C_{2v} symmetry in these native enzymes, each d orbital has the symmetry shown in Figure 7. From our results and those for the TPP system, two possibilities can be deduced depending on whether the π radical has A_2 symmetry like the OEP and OEC systems or A_1 symmetry like the TPP system. If the π radical of the enzyme has A_1 symmetry, it does not have the same symmetry as the electron-occupied d orbitals, because the d orbitals with the same symmetry, such as $d_{x^2-y^2}$ and d_{z^2}, are empty. Since all the orbitals are orthogonal, the coupling should be ferromagnetic from the results of the TPP system. On the other hand, if the π radical has A_2 symmetry, it has the same symmetry as the d_{xy} orbital. However, it is fully occupied and other half-occupied orbitals are also orthogonal to each other. Then it is deduced from the results for the six-coordinate complexes of the OEP and OEC systems that the coupling should be weakly antiferromagnetic. Experimental results of the native enzymes suggesting weak antiferromagnetic coupling support our proposal that they have orbitals of A_2 or A_{1u} symmetry.

Conclusion

In the OEP and OEC systems the Fe(III) ($S = {}^5/_2$) and the π radical ($s = {}^1/_2$) couple antiferromagnetically in the five-coordinate complexes and weakly couple antiferromagnetically in the six-coordinate ones. This is caused by the symmetry of the π radical, which is A_{1u} in these systems. And from the results for the model complexes, the symmetries of the radical orbitals of HRP compound I and MPO compound I are suggested to be A_{1u} rather than A_{2u}.

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Registry No. **1**, 130063-78-4; **2**, 100333-81-1; **3**, 130063-79-5; **4**, 130063-81-9; **5**, 130063-83-1; HRP compound I, 62628-26-6; MPO compound I, 9003-99-0.

Contribution from the Departments of Chemistry, Georgetown University, Washington, D.C. 20057,
and Northeastern University, Boston, Massachusetts 02115

Unusually Strong Antiferromagnetic Coupling in Unsymmetrical Diiron(III) μ-Oxo Complexes

Pedro Gomez-Romero,*[1a,b] E. H. Witten,[1c] William Michael Reiff,[1c] and Geoffrey B. Jameson*[1a]

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The complex [N6FeOFeCl$_3$]Cl·0.5HCl·3H$_2$O·2C$_2$H$_5$OH, where N6 is the potentially hexadentate ligand *N,N,N′,N′*-tetrakis((2-benzimidazolyl)methyl)ethanediamine, shows distinctively strong antiferromagnetic coupling (J = −126 (1) cm^{-1}), more typical of multiply bridged diiron(III) μ-oxo species than of singly bridged species. The X-ray crystal and molecular structure shows a single oxo bridge linking an octahedrally coordinated Fe(III)—one benzimidazole group of ligand N6 does not coordinate—with a tetrahedrally coordinated Fe(III). Some key metrical details are as follows: O–FeCl$_3$, 1.745 (7) Å; O–FeN6, 1.791 (7) Å; Fe–O–Fe, 153.2(4)°; average Fe–Cl 2.20 (1) Å; average Fe–N$_{Im}$, 2.08 (2) average Fe–N$_{amine}$, 2.32 (4) Å. Infrared spectroscopy reveals a strong doublet at 833 and 850 cm^{-1} that is associated with the Fe–O–Fe moiety; the latter band is assigned to ν_{as}(Fe–O–Fe). An analysis of orbital interactions reveals how low symmetry (at most, idealized C_s) can facilitate stronger antiferromagnetic coupling than occurs for more symmetrical (C_{2v}) singly bridged diiron(III) μ-oxo species. The distinctive magnetic and vibrational properties associated with these unsymmetrical species extends the range of spectroscopic behavior associated with diiron(III) μ-oxo species, with important consequences in the application of these techniques to dinuclear iron proteins. Relevant crystal and refinement data include the following: monoclinic space group $P2_1/n$; a = 13.775 (4), b = 26.911 (7), c = 13.758 (4) Å; β = 96.24 (2)°; d_{obs} = 1.28 (2), d_{calc} = 1.29 g cm^{-3} for Z = 4; 4231 retained data with $I > 0$ in the range $0.10 < \lambda^{-1} \sin\theta < 0.5399$ Å^{-1}; graphite-monochromated Mo Kα radiation (λ = 0.7107 Å); $R(F^2$, all data) = 0.19, $R_w(F^2)$ = 0.22; for the 2126 data for which $I > 3\sigma(I)$, $R(F)$ = 0.088 and $R_w(F)$ = 0.104.

Many symmetrical diiron(III) μ-oxo complexes are known.[2,3] In biological occurrences of this moiety the two iron atoms are often spectroscopically distinct in Mössbauer spectroscopy and unsymmetrical species are inferred.[3] Thus the spectroscopic, magnetic, and structural consequences of asymmetry and of

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* To whom correspondence should be addressed.

(1) (a) Georgetown University. (b) Institut de Ciencia de Materiales de Barcelona, Marti i Franques s/n, 08028 Barcelona, Spain. (c) Northeastern University.

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