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# Electronic States and Magnetic Properties of Triplet Porphyrinato Copper(II) Cation Radical Complexes

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The porphyrinato copper cation radical complexes were examined by EPR spectroscopy. The cation radical complexes having bulky peripheral substituents are present as monomers in fluid solution and show EPR spectra due to intramolecular spin coupling between the spins on copper and on the porphyrin ring. The cation radical complexes, having no such substituents, form a dimer in solution. On the other hand, when they are oxidized in frozen solution by $\gamma$-ray irradiation, the cation radical complexes are always formed as a monomer, showing a triplet state EPR due to the intramolecular spin coupling. The zero field splitting and spin exchange parameters, $|D|$ and $2J$, obtained from EPR measurements were classified into two groups by their magnitudes. The tetraphenylporphyrinato copper(II) cation radical complex, $[\mathrm{Cu^{II}(tpp)}]^+$, has a small $|D|$ and a small negative $2J$ value, while the octaethylporphyrinato copper(II) cation radical complex, $[\mathrm{Cu^{II}(oep)}]^+$, has a large $|D|$ and a large negative $2J$ value. The other porphyrinato copper(II) cation radical complexes are classified into one of these two type of complexes. These classifications can be related to the electronic configuration of the porphyrin cation radicals. These $|D|$ and $2J$ values also suggest that the triplet state monomer complexes of porphyrinato copper(II) cation must be deformed from the planar structure.

The oxidized states of metalloporphyrins participate in reactions of a variety of biological systems such as photosynthetic systems, heme peroxidases, P450 monooxygenases, and catalases.[1] Oxidation of metalloporphyrins occurs at either the metal or the porphyrin ring, or at both locations. These oxidized states play a key role in their enzymatic functions. In cases of complexes having paramagnetic centers at both the metal ion and the porphyrin ring, investigations on magnetic interactions between the paramagnetic centers seem very important to elucidate characteristic features of their electronic structure and their roles in the enzymatic functions. Such studies are also useful for development of new catalyses based on the biomimetic standpoint. On the other hand, there have been many attempts to develop new magnetic materials consisting of various magnetic molecules and ions.[2] Paramagnetic metalloporphyrins, having their paramagnetic center at the metal or porphyrin or at both locations, must be interesting magnetic molecular units for new hybrid magnetic materials. Investigations of the magnetic properties of this type of molecule seem also interesting.

There have been a lot of investigations on intramolecular spin-couplings in hemes, non-heme enzymes and their model compounds.[3] It has been shown that the compound I of horseradish peroxidase (HRP) has the spin of $S = 1$ on the central iron(IV) ion and the spin of $S = 1/2$ on the porphyrin ring; these spins weakly and antiferromagnetically couple with each other to produce an overall spin of $S = 1/2$.[4] Interactions between the central paramagnetic metal ion and the unpaired spin on the porphyrin ligand seem to be sensitively affected by various factors.[3j,5] For example, remarkably different $\mu_{\mathrm{eff}}$ values (2.88,[6] 0,[7] 2.4,[8] 2.9 $\mu_{\mathrm{B}}$[9]) have been reported for the tetraphenylporphyrinato copper(II) cation radical complex ($[\mathrm{Cu^{II}(tpp)}]^+$) in solution. The complex is EPR silent in the both frozen and fluid solutions. On the other hand, it has been reported that the octaethylporphyrinato copper(II) cation complex ($[\mathrm{Cu^{II}(oep)}]^+$), obtained by $\gamma$-ray irradiation of the frozen solution, showed a triplet state EPR spectrum, due to intramolecular spin coupling,[10] while when it was oxidized in fluid solution, the complex showed a triplet state EPR spectrum due to intermolecular copper-copper coupling at the frozen state.[11]

It seems useful to study systematically general features of magnetic properties of metalloporphyrin cation radicals having a paramagnetic ion as a central metal. There have been few investigations concerning correlation between magnetic properties of metalloporphyrin cation complexes with paramagnetic metal and electronic configurations of the porphyrin rings. In the present work, we tried to clarify the intramolecular spin–spin interactions in some porphyrinato copper(II) cation complexes and their correlation with the electronic configuration of the porphyrin ring by using EPR spectroscopy. It is known from many spectroscopic investigations that the cation radical complexes of $Cu^{II}$(tpp) and $Cu^{II}$(oep) have different electronic configurations.[12] In the present work we used the cation radical complexes of $Cu^{II}$(tpp), $Cu^{II}$(oep), and their related complexes as shown in Fig. 1.

## Experimental

**Materials.** Tetraphenylporphyrin ($H_2$tpp), octaethylporphyrin ($H_2$oep), mesoporphyrin-IX-dimethylester ($H_2$mp), and tetrakis(*p*-methoxyphenyl)porphyrin ($H_2$(*p*-$OCH_3$)tpp) were obtained commercially. Tetrakis(pentafluorophenyl)porphyrin ($H_2$pfpp), tetramesityl-porphyrin ($H_2$tmp), and the *p*-chlorophenyl-, *o*-fluorophenyl-, *o,o′*-dichlorophenyl-, and *o,o′*-difluorophenyl derivatives of $H_2$tpp, ($H_2$(*p*-Cl)tpp, $H_2$(*o*-F)tpp, $H_2$dcpp, and $H_2$dfpp) were prepared by the previously published method.[13] These porphyrins were converted to copper(II) complexes by the method of Adler et al.[14]

Tetrabutylammonium perchlorate (TBAP), which was used as a supporting electrolyte in electrolysis, was recyrstallized from ethanol and dried in vacuo at 70 °C. Dichloromethane (DCM) used as a solvent was distilled over $CaH_2$ and stored over 4 Å molecular sieves in an ampule on a vacuum line. Commercially obtained GR grade 1,1′,2,2′-tetrachloroethane (TCE) and fluorobenzene were used as solvents without further purification.

The porphyrinato copper(II) complexes were oxidized by the following three methods or by a combination of them; 1) electrochemical oxidation by use of TBAP as a supporting electrolyte in DCM, 2) chemical oxidation with phenyloxathiinylium hexachloroantimonate in DCM or fluorobenzene, and 3) oxidation by $\gamma$-ray irradiation in frozen TCE matrix. All the sample solutions were degassed by a vacuum line prior to oxidation. The concentration of the complex for all solutions was about $1\times10^{-3}$ mol dm$^{-3}$.

**EPR Measurements.** Frozen state EPR spectra were recorded on a Varian E112 spectrometer at temperatures below 77 K. The temperatures were controlled by the helium gas flow type Oxford cryostat. The magnetic fields and microwave frequencies were measured by an Echo EFM-2000 NMR field meter and a Takeda Riken TR-5501 frequency counter, respectively.

## Results

The $[Cu^{II}(oep)]^+$ complex obtained by the chemical or electrolytic oxidation in fluid solution gave a triplet state EPR spectrum with a seven line hyperfine (hf) splitting in the $\Delta M$s = 2 transition in the frozen state (Fig. 2). The observed seven-line hf-splitting of an average separation of 9.1 mT is attributable to the interaction with two copper nuclei. The same spectrum has been observed by Mengersen et al.[11] for this system. As they reported, this spectrum can be ascribed to formation of a face to face dimer of $[Cu^{II}(oep)]^+$; in the dimer, the unpaired spins on the porphyrin rings are antiferromagnetically coupled by intermolecular $\pi$–$\pi$ interaction, and the intermolecular copper–copper coupling $J_{dd}$ gives the triplet state EPR spectrum. On the other hand, when the $Cu^{II}$(oep) complex was oxidized in the frozen state by $\gamma$-ray irradiation, the oxidized complex showed a triplet EPR signal with a quartet hf splitting in the $\Delta M$s = 2 transition, which is due to a coupling with the single copper nucleus (Fig. 3).[10] This type of spectral pattern can be assigned to a triplet monomer, as will be shown in more detail in the following examples.

In contrast to $[Cu^{II}(oep)]^+$, oxidation of $Cu^{II}$(tmp) by chemical oxidation in fluid solution gave a frozen state EPR

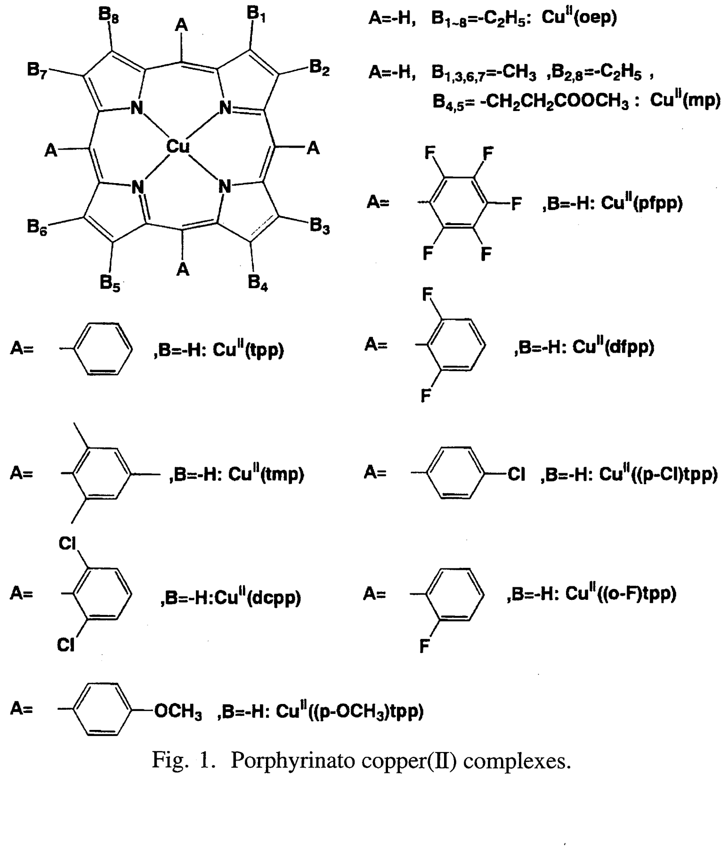

Fig. 1. Porphyrinato copper(II) complexes.

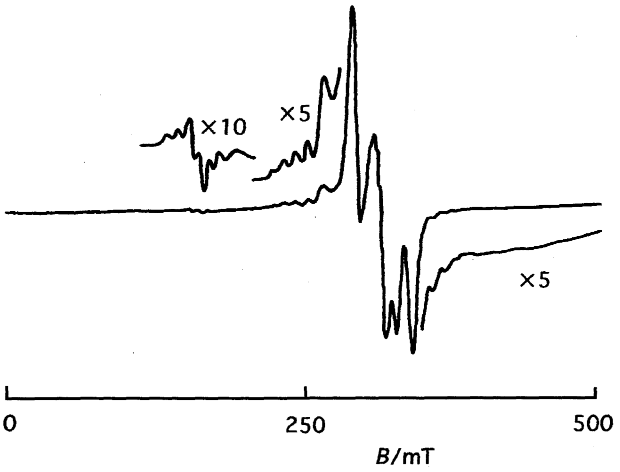

Fig. 2. Frozen solution EPR spectrum of $[\mathrm{Cu^{II}(oep)}]^+$ produced by chemical oxidation of fluid DCM solution, showing formation of $([\mathrm{Cu^{II}(oep)}]^+)_2$ dimer. The spectrum was recorded at 77 K.

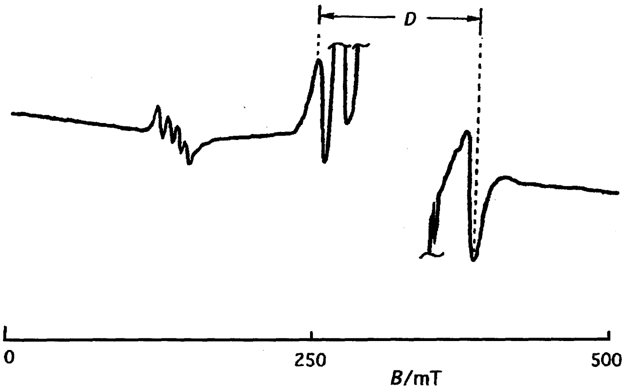

Fig. 3. Frozen solution EPR spectrum of $[\mathrm{Cu^{II}(oep)}]^+$ monomer produced by $\gamma$-ray irradiation of frozen TCE solution. The spectrum was recorded at 77 K.

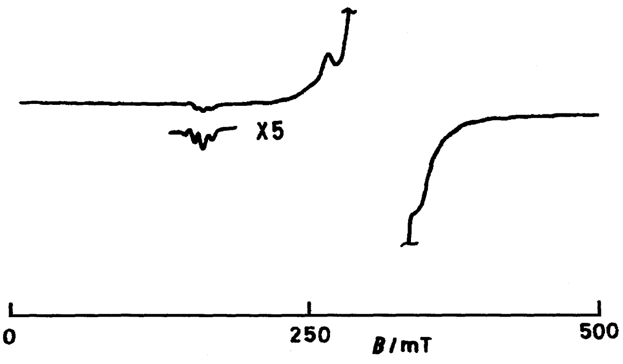

Fig. 4. Frozen solution EPR spectrum of $[\mathrm{Cu^{II}(tmp)}]^+$ produced by chemical oxidation of fluid DCM solution. The spectrum was recorded at 77 K.

spectrum (Fig. 4) similar to that of the $[\mathrm{Cu^{II}(oep)}]^+$ oxidized by $\gamma$-ray irradiation in the frozen state. The spectral pattern is of a typical triplet state[15] and the peak at the magnetic field region of $g = 2$ can be ascribed to the perpendicular components of the $\Delta M\mathrm{s} = 1$ transitions. The signals centered at about 155 mT in the spectrum are assigned to the $\Delta M\mathrm{s} = 2$ transitions and the observed four line hf splittings with an average separation of 8.7 mT in this low field region are attributed to the hf coupling with a single copper nucleus. These features indicate formation of a triplet state monomer with the intramolecular coupling between the spins on copper and the porphyrin ring. The zero field splitting parameters $|D|$ and $|E|$ were obtained as ca. 0.04 $\mathrm{cm^{-1}}$ and ca. 0 $\mathrm{cm^{-1}}$, respectively, by computer simulation of the spectrum using a program written based on the second order perturbation method for the Hamiltonian containing g tensor, zero-field splitting tensor, and copper hf coupling tensor in an arbitrary tensor orientation.[16]

The frozen solutions of the $[\mathrm{Cu^{II}}((o\text{-F})\mathrm{tpp})]^+$, $[\mathrm{Cu^{II}(dfpp)}]^+$, $[\mathrm{Cu^{II}(dcpp)}]^+$, and $[\mathrm{Cu^{II}(pfpp)}]^+$ radical complexes generated by the electrochemical oxidation also showed triplet state monomer EPR spectra similar to those observed for $[\mathrm{Cu^{II}(tmp)}]^+$ and $[\mathrm{Cu^{II}(oep)}]^+$ (Fig. 5). Oxidation of $\mathrm{Cu^{II}tpp}$ and $\mathrm{Cu^{II}}(p\text{-X})\mathrm{tpp}$ (X = Cl, $\mathrm{OCH_3}$) by the electrochemical oxidation in fluid solution state did not give any EPR spectra at frozen state, but when they were oxidized by $\gamma$-radiolysis in the frozen TCE matrix they gave a triplet state monomer EPR spectrum (Fig. 6).

The $|D|$ values obtained from the EPR spectra for the triplet state monomer porphyrinato copper(II) cation complexes are summarized in Table 1. For the complexes having a $|D|$ value smaller than 0.05 $\mathrm{cm^{-1}}$, the computer simulation of the spectrum is not necessarily effective because of overlap of the signals coming from the unoxidized copper complex. In such cases only the upper limit of the $|D|$ value is shown. Meanwhile, the $2J$ values were determined from the temperature dependence of the signal intensities of the $\Delta M\mathrm{s} = 2$ transitions by using the following Bleaney–Bower equation:[17]

$$\frac{I(T)}{I(T')} = \frac{T'\{3+\exp(-2J/kT')\}}{T\{3+\exp(-2J/kT)\}}, \tag{1}$$

where $I(T)$ and $I(T')$ are EPR intensities at temperatures $T$ and $T'$, respectively, and $k$ is the Boltzmann constant. As Fig. 7 shows, the signal intensities of $[\mathrm{Cu^{II}(oep)}]^+$ and $[\mathrm{Cu^{II}(pfpp)}]^+$ decrease at low temperatures while those of $[\mathrm{Cu^{II}(tpp)}]^+$, $[\mathrm{Cu^{II}}((p\text{-Cl})\mathrm{tpp})]^+$, and $[\mathrm{Cu^{II}}((p\text{-OCH_3})\mathrm{tpp})]^+$ increase from

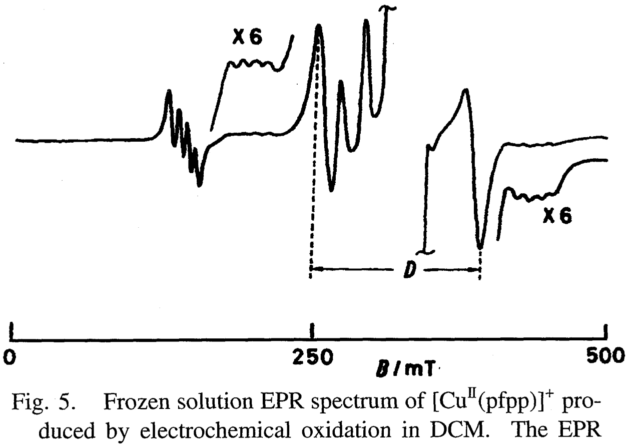

Fig. 5. Frozen solution EPR spectrum of $[\mathrm{Cu^{II}(pfpp)}]^+$ produced by electrochemical oxidation in DCM. The EPR spectrum was recorded at 77 K.

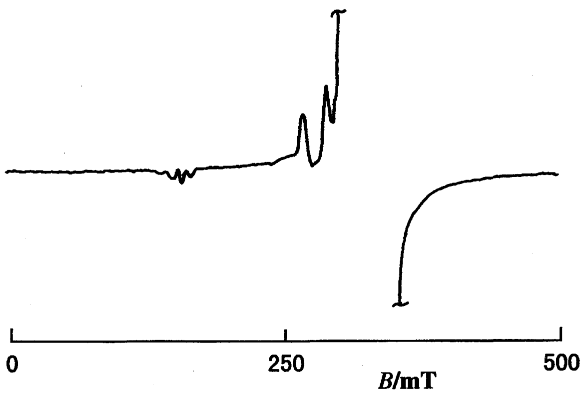

Fig. 6. Frozen solution EPR spectrum of [Cu$^{II}$(tpp)]$^+$ monomer produced by $\gamma$-ray irradiation of frozen TCE solution. The spectrum was recorded at 77 K.

Table 1. EPR Parameter of the Porphyrin Copper(II) Cation Complexes

| Complexes | $\lvert D\rvert$/cm$^{-1}$ | $2J$/cm$^{-1}$ |
|---|---|---|
| [Cu$^{II}$(oep)]$^+$ | 0.116 | −93 |
| [Cu$^{II}$(mp)]$^+$ | 0.115 | −100 |
| [Cu$^{II}$(pfpp)]$^+$ | 0.118 | −32 |
| [Cu$^{II}$(dfpp)]$^+$ | 0.115 | −20 |
| [Cu$^{II}$(tmtmp)]$^+$ a) | 0.116 | −140 |
| [Cu$^{II}$(tpp)]$^+$ | ca. 0.04 | −4 |
| [Cu$^{II}$(tmp)]$^+$ | ca. 0.04 | −1 |
| [Cu$^{II}$((*p*-Cl)tpp)]$^+$ | ca. 0.04 | −3 |
| [Cu$^{II}$((*p*-OCH$_3$)tpp)]$^+$ | ca. 0.04 | −2 |
| [Cu$^{II}$((*o*-F)tpp)]$^+$ | ca. 0.04 | −3 |
| [Cu$^{II}$(dcpp)]$^+$ | ca. 0.04 | −5 |

a) Ref. 21b, tmtmp = 2, 7, 12, 17- tetramethyl- 3, 8, 13, 18- tetramesitylporphyrinato.

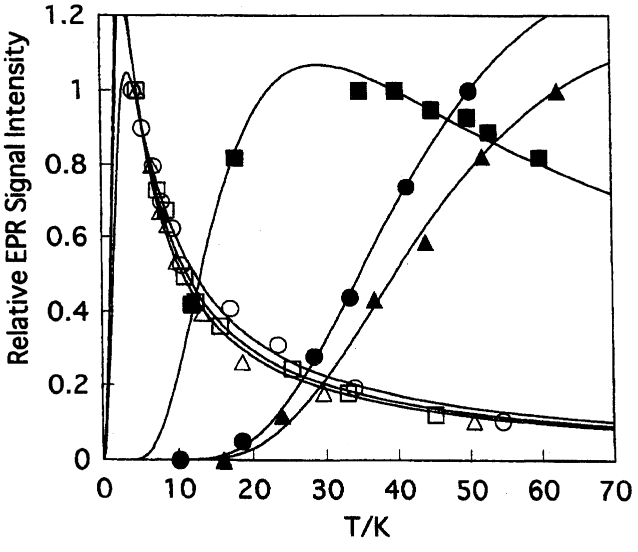

Fig. 7. Temperature dependence of relative EPR signal intensities of $\Delta Ms = 2$ transition: ●, [Cu$^{II}$(oep)]$^+$; ■, [Cu$^{II}$(pfpp)]$^+$; ▲, [Cu$^{II}$mp]$^+$; ○, [Cu$^{II}$(tpp)]$^+$; □, [Cu$^{II}$((*p*-Cl)tpp)]$^+$; △, [Cu$^{II}$((*p*-OCH$_3$)tpp)]$^+$; The solid lines were obtained by non-linear least square fitting of the Bleaney–Bower equation.

50 to 5 K. The solid lines in Fig. 7 were obtained by non-linear least square fitting of the Bleaney–Bower equation to relative EPR intensities. In the fitting, the experimentally observed maximum EPR intensity and the temperature giving its intensity $T'$ were taken as references in the Bleaney–Bower equation, and relative EPR intensities were normalized by the maximum intensity. The $2J$ values determined by the fitting procedure are listed in Table 1.

## Discussion

**Dimer Formation of the Radical Complexes in Solution.** As stated above, the cation radical of Cu$^{II}$(oep) forms a dimer in fluid solution. Mengersen et al. explained the observed triplet state EPR spectrum by intermolecular copper-copper coupling. The porphyrin–porphyrin $\pi$–$\pi$ exchange interaction $J_{\pi\pi}$ was considered to be large and antiferromagnetically coupled, and $J_{\pi\pi} < J_{d\pi}$.[11,18]

On the other hand, [Cu$^{II}$(tpp)]$^+$ and [Cu$^{II}$(*p*-X)tpp]$^+$ showed triplet state monomer EPR signals when they were oxidized in the frozen TCE matrix by $\gamma$-ray irradiation, while they did not give any EPR signals when they were oxidized in fluid solution. Previously, Scholz et al. reported that the [Cu$^{II}$(tpp)]$^+$ complex crystal, where the complex is in a dimer form, is EPR silent.[6] In the dimer, [Cu$^{II}$(tpp)]$^+$ is distorted from planar and the spins on the copper and porphyrin ring were considered to be antiferromagnetically coupled by the overlap of the unpaired spin orbitals. In the present case, the complexes of [Cu$^{II}$(tpp)]$^+$ and [Cu$^{II}$(*p*-X)tpp]$^+$ produced in the fluid solution are considered to form dimers in solution. In contrast to the case of [Cu$^{II}$(oep)]$^+$, the distortion of the [Cu$^{II}$(tpp)]$^+$ and [Cu$^{II}$(*p*-X)tpp]$^+$ molecules in the fluid solutions from planar may be large in the dimer because of the presence of the phenyl groups. Then intramolecular $J_{d\pi}$ would become large, resulting in EPR inactivity by antiferromagnetic coupling. The [Cu$^{II}$(tpp)]$^+$ complexes oxidized in the frozen matrix by $\gamma$-ray irradiation inhibit formation of the dimer, so their complexes are EPR active.

The [Cu$^{II}$(tpp)]$^+$ complexes with O-substituted phenyl group such as [Cu$^{II}$(tmp)]$^+$, [Cu$^{II}$(pfpp)]$^+$, [Cu$^{II}$((*o*-F)tpp)]$^+$, [Cu$^{II}$(dfpp)]$^+$, and [Cu$^{II}$(dcpp)]$^+$ inhibit formation of the dimer by the presence of the ortho-substituted phenyl groups which would orient perpendicularly to the porphyrin ring.[19] They are EPR active even when they are produced in fluid solution.

**Isotropic Exchange Interaction Parameter 2*J*.** One can see from Table 1 that the radical complexes can be classified into two groups by the magnitudes of the $\lvert D\rvert$ and $2J$ values; the radical complexes having large $\lvert D\rvert$ and large negative $2J$ values and the ones having small $\lvert D\rvert$ and small negative $2J$ values. The former class includes [Cu$^{II}$(oep)]$^+$ and its relating compounds and the latter includes [Cu$^{II}$(tpp)]$^+$ and its substituted derivatives. Exceptionally, the complexes of tetraphenylporphyrin with strong electron withdrawing substituents such as [Cu$^{II}$(pfpp)]$^+$ and [Cu$^{II}$(dfpp)]$^+$ are included in the former. It is well known that cation radicals of metalloporphyrins of tpp and oep have different electronic configurations; the former usually has an unpaired spin in the $a_{2u}$ type orbital and the latter has an unpaired spin in the $a_{1u}$ type one.[12c,12e,20] In $[Cu^{II}(pfpp)]^+$ and $[Cu^{II}(dfpp)]^+$, the electron withdrawing substituents at the meso positions will stabilize the $a_{2u}$ type orbital which is closely located to the $a_{1u}$ type orbital so that the $a_{1u}$ type orbital may become a half-filled level as in the oep type complexes. Such a substituent effect has been discussed previously in some porphyrin complexes.[5c,21] It seems likely, therefore, that the differences in the $|D|$ and $2J$ values are strongly related to the difference in the electronic configurations of the porphyrin cations; the complexes having the $A_{2u}$ type electronic configuration would have small negative $2J$ and $|D|$ values and those of the $A_{1u}$ type would have large negative $2J$ and $|D|$ values.

We consider here factors that contribute to the observed $2J$ values. In general, orthogonality between the magnetic orbitals of the two paramagnetic centers is an important factor to $2J$; it relates to potential exchange and kinetic exchange effects, the former giving a positive $2J$ value and the latter giving a negative one.[22] On the other hand, the spin polarization effect sometimes makes an appreciable contribution to $2J$.[22] We consider first this spin polarization effect, because it strongly relates to the electronic configuration of the paramagnetic centers.

The $a_{2u}$ type unpaired electron orbital has large electron spin densities on the nitrogens and the *meso*-carbons. The spin polarization effect induces up spin density on the nitrogen lone-pair orbital for the Cu–N bonding by the large up spin density on the nitrogen π orbital. The induced spin is parallel to the spin of the copper $d_{x^2-y^2}$ unpaired spin orbital in the Cu–N direction. Such spin alignment will contribute to the ferromagnetic interaction, i.e., a positive $2J$ value.

On the other hand, the unpaired electron orbital in the $A_{1u}$ type radicals has a node on nitrogen and down spin densities may be induced on the nitrogen π orbital by the large up spin densities on the neighbor carbon π orbitals. This down spin density on the nitrogen π will, in the reverse manner to that in the $A_{2u}$ type radicals, contribute to antiferromagnetic interaction, i.e., a negative $2J$ value.

Table 1 shows that both the oep and tpp type complexes have negative $2J$ values, though $2J$ for the tpp type complexes are small. There negative $2J$ vales obtained in the tpp type complexes suggest that the kinetic exchange effect must be making some contribution to $2J$ in this system. The kinetic exchange contribution comes from overlap between the two magnetic centers. For the ttp type complexes with $d_{x^2-y^2}$ metal magnetic site and the $a_{2u}$ type radical site, such overlap is caused by distribution of the complex molecules to a non-planar $S_4$ or $D_{2d}$ symmetry structure, i.e., distortion to a saddle like structure where the two nitrogens facing each other shift up from the molecular plane and the other two nitrogens shift down from the plane. In the oep type complexes, it is not clear from only the $2J$ values whether the kinetic exchange effect is contributing to $2J$ or not. Distortion of the molecular structure in the oep type complexes will be mentioned later.

**Zero-Field Splitting Parameter $|D|$.** The zero-field splitting parameter $|D|$ has two origins.[23] One is the magnetic dipole–dipole interaction between the unpaired spins ($D_{dip}$), and the other is contribution from the orbital angular momentum coming from the spin–orbit couplings ($D_{so}$).

$D_{dip}$ can be calculated if the spin distribution is known. In the present work, we evaluated $D_{dip}$ by using a spin distribution obtained by the extended Hückel MO calculations and by the following half point dipole approximation:

$$D_{k,\mathrm{dip}} = g^2\beta^2 \sum\sum Q_i Q_j \frac{r_{ij}^2 - 3X_{kij}^2}{r_{ij}^5}. \qquad (k = x, y, z) \tag{2}$$

In Eq. 2, $Q_i$ and $Q_j$ are the spin densities on one of the orbital lobes of the *i*th atom on the porphyrin ligand and those on the *j*th orbital lobe of the copper $d_{x^2-y^2}$ orbital, $r_{ij}$ is the distance between the *i*th and *j*th orbital lobes, and $X_{kij}$ is relative coordinates between the *i*th and the *j*th orbital lobes along the $k$ ($k = x$, $y$, or $z$) axis, respectively. The summation is taken for all the porphyrin π and copper $d_{x^2-y^2}$ orbital lobes. $D_{dip}$ were calculated to be +0.045 cm$^{-1}$ for $[Cu^{II}(tpp)]^+$ and +0.033 cm$^{-1}$ for $[Cu^{II}(oep)]^+$.

The absolute values of the calculated $D_{dip}$ for the $[Cu^{II}(oep)]^+$ type are smaller than the experimental $|D|$, suggesting that $D_{so}$ makes an appreciable contribution to $|D|$. By using the relation $D_{x,so}+D_{y,so}+D_{z,so} = 0$, $\Delta g_{//} = g_{//} - g_e = 2\xi|<\phi_g|l_z|\phi_{xy}>|^2/\Delta E_{xy}$, $\Delta g_{\perp} = g_{\perp} - g_e = 2\xi|<\phi_g|l_y|\phi_{xz}>|^2/\Delta E_{xz}$, and the $g$-values of the porphyrinato copper(II), $g_{//} = 2.19$ and $g_{\perp} = 2.05$, $D_{so}$ can be expressed as

$$D_{x,so} = D_{y,so} = 0.0015J_{xy} - 0.0004J_{xz}, \tag{3}$$

$$D_{z,so} = -0.0030J_{xy} + 0.0008J_{xz}. \tag{4}$$

In these equations, the $2J_{xy}$ and $2J_{xz}$ are $2J$ values in the locally excited states where the unpaired spin of the metal occupies the copper $d_{xy}$ or $d_{xz}$ orbital, respectively. In these locally excited states, the $d_{xz}$ orbital does not overlap with the porphyrin unpaired electron orbital by their symmetry even when the molecules are deformed to a non-planar structure. Hence $2J_{xz}$ would be positive. On the other hand, the $d_{xy}$ orbital overlaps with the ligand unpaired spin orbital under the non-planar distortion of the molecules, and hence $J_{xy}$ may be negative. So, it is likely that $D_{z,so}$ is positive and hence $D$ is positive. From the experimental $|D|$ and the calculated $D_{dip}$, $D_{so}$ are estimated to be ca. 0.0 and ca. 0.10 cm$^{-1}$ for the $A_{2u}$ and the $A_{1u}$ type complexes, respectively. Overlap of the $d_{xy}$ orbital with the $a_{1u}$ type porphyrin orbital occurs when the complex molecules distort to the non-planar saddle-like structure where the two coordinating nitrogens facing each other shift up from the molecular plane and the other two nitrogens shift down from the plane. Such distortion of the molecules does not contribute to overlap between the copper $d_{xy}$ orbital and the porphyrin $a_{2u}$ type orbital. The larger $D_{so}$ in the $A_{1u}$ type complexes may be due to such an effect of the orbital overlap by the distortion of the molecules.

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