

# Characterization and Intramolecular Spin Coupling of a Monomeric $a_{1u}$ Copper(II) Porphyrin $\pi$ -Cation Radical

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The intramolecular magnetic interaction between copper(II) and  $a_{1u}$  porphyrin radical spins in  $[\text{Cu}(\text{TMTMP}^+)]\text{[SbCl}_6\text{]}^-$  ( $\text{TMTMP}^+ = \pi$ -cation radical of 2,7,12,17-tetramethyl-3,8,13,18-tetramesitylporphyrin) was investigated by using ESR measurements in frozen dichloromethane and by solid magnetic susceptibility measurements. The monomeric nature of  $[\text{Cu}(\text{TMTMP}^+)]\text{[SbCl}_6\text{]}^-$  at low temperature was confirmed by low-temperature UV-visible absorption spectral measurements. The radical orbital occupancy of  $[\text{Cu}(\text{TMTMP}^+)]\text{[SbCl}_6\text{]}^-$  was examined by use of hyperfine-shifted deuterium NMR resonances, which showed characteristics of an  $a_{1u}$  radical state. The ESR spectrum of  $[\text{Cu}(\text{TMTMP}^+)]\text{[SbCl}_6\text{]}^-$  afforded signals having characteristics of a monomeric triplet state; i.e., the signal was separated into a four-line component from the interaction of a single copper(II) center and a pair of signals in high field. The temperature dependence of the ESR spectra of  $[\text{Cu}(\text{TMTMP}^+)]\text{[SbCl}_6\text{]}^-$  signifies the  $S = 0$  ground state (antiferromagnetic). The solid magnetic susceptibility measurements for  $[\text{Cu}(\text{TMTMP}^+)]\text{[SbCl}_6\text{]}^-$  demonstrated antiferromagnetic coupling between copper(II) and  $a_{1u}$  radical spins with  $J = -120 \text{ cm}^{-1}$ . Antiferromagnetic coupling in  $[\text{Cu}(\text{TMTMP}^+)]\text{[SbCl}_6\text{]}^-$  can be explained by the spin density at the pyrrole nitrogen atom in the  $a_{1u}$  radical orbital.

## Introduction

Metalloporphyrin  $\pi$ -cation radicals with paramagnetic metal ions, such as copper(II),<sup>1-3</sup> iron(III),<sup>2,4</sup> and manganese(III),<sup>5</sup> have been shown to exhibit spin coupling between the paramagnetic metal and ligand  $\pi$ -radical spins. Many studies on spin coupling of metalloporphyrin  $\pi$ -cation radical species have recently been reported by Reed et al.<sup>6-8</sup> They observed that the coupling of high-spin iron(III) and ligand spins is antiferromagnetic in ruffled porphyrins and ferromagnetic in planar porphyrins.<sup>7,9</sup> On the basis of this finding, they offered a theory involving the occupations and symmetries of the orbitals in the metal and the ligand that contain unpaired electrons.

As in the iron(III) porphyrin  $\pi$ -cation radical species discussed above, spin coupling in copper(II) porphyrin  $\pi$ -cation species has also been the focus of recent research.<sup>8,10</sup> However, the observed magnetic data on copper(II) porphyrin  $\pi$ -cation radical species have presented a confusing picture because of the intermolecular antiferromagnetic coupling caused by association into dimeric units.<sup>1-3,11</sup> The ESR spectrum of the copper(II) octaethylporphyrin, Cu(OEP),  $\pi$ -cation radical showed characteristics of a dimeric copper(II) triplet state, and the seven-line, 100 G hyperfine structure in the 1800 G region confirmed the interaction of two copper centers.<sup>10,12</sup> A monomeric triplet ESR spectrum of the Cu(OEP)  $\pi$ -cation radical has been detectable only when the

radical species is produced in a tetrachloroethane matrix at 77 K by  $\gamma$  radiolysis.<sup>13</sup> Recently, Erler et al. succeeded in preparing the monomeric copper(II) porphyrin  $\pi$ -cation radical species by preventing the direct association of the radical species.<sup>8</sup> They reported strong ferromagnetic coupling between copper(II) and ligand radical spins in the copper(II) 5,10,15,20-tetramesitylporphyrin, Cu(TMP),  $\pi$ -cation radical.

However, an important caveat is that these findings are in metalloporphyrin  $\pi$ -cation radicals which have an  $a_{2u}$  radical character. There have been only a few reports on intramolecular spin coupling between metal and ligand radical spins in  $a_{1u}$  metalloporphyrin  $\pi$ -cation radicals. In the previous study of the Cu(TMP)  $\pi$ -cation radical, weak ferromagnetic coupling was predicted for  $a_{1u}$  metalloporphyrin  $\pi$ -cation radical species having  $D_{4h}$  symmetry.<sup>8</sup> We recently studied the magnetic properties of iron(III) porphyrin and chlorin  $\pi$ -cation radicals with  $a_{1u}$  radical character and found notable differences between the spin coupling in  $a_{1u}$  and the  $a_{2u}$  radical complexes.<sup>14</sup> Even more recently, however, more complicated features have been reported in Fe-(OEP)  $\pi$ -cation radical species,<sup>15</sup> and the relative magnitudes of the coupling between metal spins in  $a_{1u}$  and  $a_{2u}$  radicals remains uncertain.

We report here the characterization and the magnetic properties of monomeric  $a_{1u}$  copper(II) porphyrin  $\pi$ -cation radical species by using absorption spectra, NMR, ESR, and magnetic susceptibility measurements. To obtain the  $a_{1u}$  radical species, and to prevent the dimer formation of  $\pi$ -radical species, we synthesized the (2,7,12,17-tetramethyl-3,8,13,18-tetramesitylporphyrinato)-copper(II) complex, Cu(TMTMP). Substitution at the pyrrole  $\beta$ -position, such as in ethioporphyrin (EtioP), was expected to produce the  $a_{1u}$  radical species. The mesityl group at the pyrrole  $\beta$ -position would effectively isolate the  $\pi$ -cation radical molecule from even weak intermolecular interactions, as has been reported for the Cu(TMP) analogue. Oxidation produced the monomeric  $a_{1u}$   $\pi$ -radical species in dichloromethane solution and in the solid state, even at low temperature. We also demonstrate the

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antiferromagnetic coupling between copper(II) and a  $1u$  radical spins, which is discussed in relation to the spin distribution of  $a_{1u}/a_{2u}$  orbitals.

### Experimental Section

**Physical Measurements.** Electronic spectra were recorded on a Hitachi U-3200 spectrometer. Proton NMR spectra at 400 MHz and deuterium NMR spectra at 61.4 MHz were recorded on a Bruker MSL-400 spectrometer. Chemical shifts were referenced to TMS, and downfield shifts were given a positive sign. The sample concentrations for proton and deuterium NMR measurements were 3–10 mM. Electron paramagnetic resonance measurements were made on a Varian E-112 spectrometer equipped with an Air Products, Ltd., low-temperature system at the Instrument Center, Institute for Molecular Science.

**Materials.** Dichloromethane and hexane were refluxed over calcium hydride for 3 h and then distilled. Phenoxathiin hexachloroantimonate salt (Phenox-SbCl<sub>6</sub>) was prepared by the published procedure.<sup>16</sup> Deuterated solvents were purchased from Aldrich and used without further purification. 5,10,15,20-Tetramesitylporphyrin (TMP) was synthesized by the usual method.<sup>17</sup> 2,7,12,17-Tetramethyl-3,8,13,18-tetramesitylporphyrin (TMTMP) was also prepared by the literature methods.<sup>18</sup> *meso-d*<sub>4</sub>-TMTMP was prepared from deuterated 2-(hydroxymethyl)-3-mesityl-4-methylpyrrole, which was obtained by the reduction of 2-(ethoxycarbonyl)-3-mesityl-4-methylpyrrole with LiAlD<sub>4</sub>, and acetic acid-*d*<sub>1</sub>. Copper was inserted into porphyrins by refluxing in chloroform with copper acetate.<sup>19</sup> Copper complexes were purified by silica gel column and recrystallized from chloroform-methanol.

**Chemical Oxidations.** Copper porphyrins and 1.1 equiv of Phenox-SbCl<sub>6</sub> were stirred in dichloromethane for 1 h, and the solution was then filtered. After evaporation, samples were redissolved in dichloromethane. Hexane was slowly added to the solution, and the solution was left to stand for 3 days. The product was separated by filtration, washed with hexane, and then dried in vacuo.

**[Cu(TMP<sup>•</sup>)]SbCl<sub>6</sub>.** UV [ $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>): 659, 409 (Soret) nm. Anal. Calcd for C<sub>56</sub>H<sub>52</sub>CuCl<sub>6</sub>N<sub>4</sub>Sb: C, 57.04; H, 4.45; N, 4.75. Found: C, 57.13; H, 4.93; N, 4.68.

**[Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub>.** UV [ $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>): 609, 560, 386 (Soret) nm. Anal. Calcd for C<sub>60</sub>H<sub>60</sub>CuCl<sub>6</sub>N<sub>4</sub>Sb: C, 58.34; H, 4.90; N, 4.54. Found: C, 58.83; H, 5.43; N, 4.87.

**Magnetic Susceptibility.** Magnetic susceptibility measurements were conducted using a microcomputer-controlled magnetic torsion balance at the Instrument Center, Institute for Molecular Science, and the Faraday method to measure the susceptibilities from 2.0 to 270 K. Microcrystalline powder samples of 25–30 mg were used. Diamagnetic corrections ( $\chi_{\text{dia}}$ ) were calculated by using the published value for the constitutive correction for H<sub>2</sub>TPP.<sup>20</sup>

### Results

**Electronic Spectra.** The chemical oxidation of Cu(TMTMP) with Phenox-SbCl<sub>6</sub> was monitored with absorption spectroscopy. Upon addition of Phenox-SbCl<sub>6</sub>, the absorption spectrum of Cu(TMTMP) acquired clear isosbestic points. Figure 1 shows the absorption spectra of Cu(TMTMP) and its one-electron oxidation product, [Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub>. The oxidized complex exhibits characteristics of metalloporphyrin  $\pi$ -cation radicals: broad  $\alpha, \beta$  bands, a new absorption around 610 nm, and the blue-shifted Soret band with a loss of intensity. The features of the absorption spectrum of [Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub> differ slightly from those of the Cu(OEP)  $\pi$ -cation radical.<sup>1</sup>

It has been reported that the Cu(OEP)  $\pi$ -cation radical readily forms a dimer in solution at low temperature.<sup>10</sup> To examine this dimer formation, we measured the low-temperature absorption spectrum of [Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub> in dichloromethane. The features of the absorption spectrum did not change at -80 °C, and a broad absorption around 800 nm, which would have been

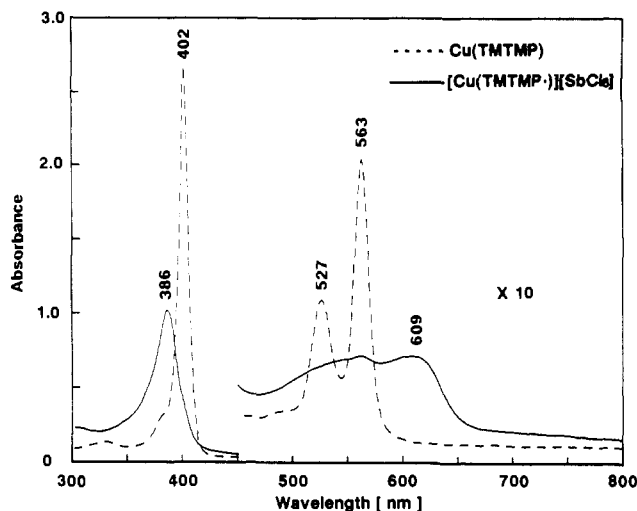


Figure 1. UV-visible absorption spectra of Cu(TMTMP) (---) and [Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub> (—) in dichloromethane.

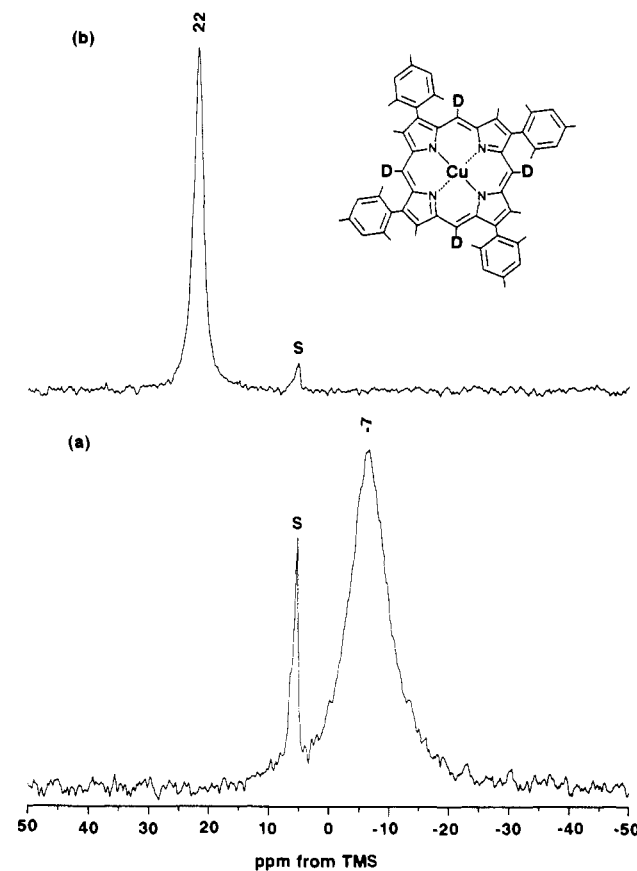


Figure 2. Deuterium NMR spectra of (a) *meso-d*<sub>4</sub>-Cu(TMTMP) and (b) *meso-d*<sub>4</sub>-[Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub> in dichloromethane at 23 °C.

attributed to the dimer, was not observed.<sup>11</sup> The dimerization of [Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub> is apparently inhibited by the steric hindrance of the pyrrole  $\beta$ -mesityl group.

**NMR Spectra.** The deuterium NMR spectra of *meso-d*<sub>4</sub>-Cu(TMTMP) and *meso-d*<sub>4</sub>-[Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub> are shown in Figure 2. The *meso* deuterium signal in Cu(TMTMP) is observed at -7 ppm. Upon oxidation, the *meso* deuterium signal is shifted downfield to 22 ppm and the line width of this peak is less than that of the parent species. The small downfield shift of the *meso* deuterium signal with oxidation suggests the negative spin density of the *meso* carbon, which arises from the electron correlation effect. The proton NMR spectrum of [Cu(TMTMP<sup>•</sup>)]SbCl<sub>6</sub> showed broad paramagnetic signals. After comparison with the previous NMR result for [Cu(OEP<sup>•</sup>)]ClO<sub>4</sub>,<sup>10</sup> the pyrrole

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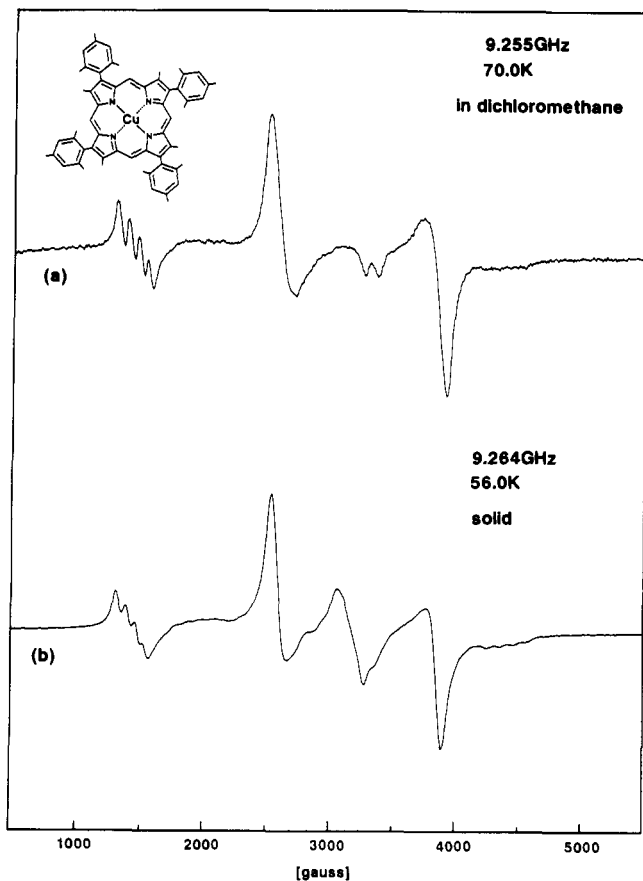


Figure 3. X-band ESR spectra of [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>]: (a) in dichloromethane at 70 K; (b) in the solid state at 56 K.

$\beta$ -methyl signal was assigned to the rather broad peak at around 30 ppm, and pyrrole  $\beta$ -mesityl protons were observed at 6.5 ppm (*o*-methyl) and 4.3 ppm (*p*-methyl). All of these features of the NMR spectra indicate an  $a_{1u}$  radical state in [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>].

**ESR Spectra.** The ESR spectrum of [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>] in frozen dichloromethane at 70 K is shown in Figure 3a. The ESR spectrum shows three major peaks at 1444, 2531, and 3882 G, which are characteristic of ESR spectra for triplet species.<sup>21</sup> The spectrum also closely resembles that of the Cu(OEP)  $\pi$ -cation radical, which was prepared by  $\gamma$  irradiation of Cu(OEP) in a tetrachloromethane matrix.<sup>13</sup> The paired high-field and low-field signals can be attributed to the  $\Delta m_s = 1$  and  $\Delta m_s = 2$  transitions, respectively. The splitting of the  $\Delta m_s = 2$  transition into four lines with an average separation of 74 G can be attributed to the hyperfine structure due to the copper nucleus ( $I = 3/2$ ). The presence of these four lines of the  $\Delta m_s = 2$  transition signal indicates that this ESR spectrum is due to the intramolecular spin coupling of the monomeric copper porphyrin  $\pi$ -cation radical. The perpendicular component of the  $g$  tensor from the midpoint between the pairs of signals is evaluated as 2.064. This value is very close to the perpendicular component of the  $g$  tensor of Cu(TMTMP). The  $D$  value, which is a zero-field splitting parameter, can be derived from the position of the  $\Delta m_s = 2$  transition. The calculated  $D$  value is  $0.1157 \text{ cm}^{-1}$ , which is almost identical to the value ( $0.1158 \text{ cm}^{-1}$ ) for the Cu(OEP)  $\pi$ -cation radical.<sup>13</sup>

An identical ESR spectrum can be obtained in solid [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>], as shown in Figure 3b. The signals attributed to the triplet state are observed at the same position as those in frozen dichloromethane. This also indicates that, even in the solid state, the dimerization of [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>]

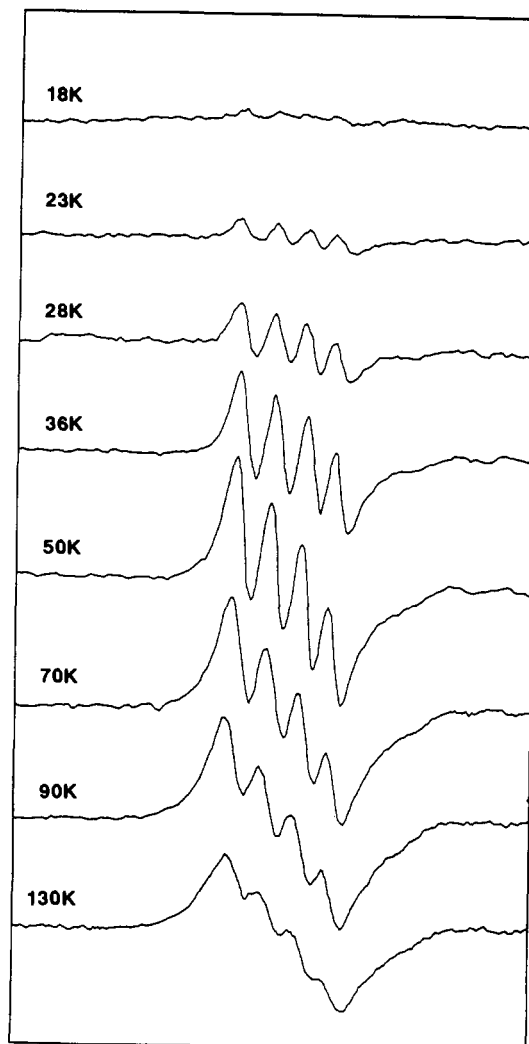


Figure 4. Temperature dependence of the  $\Delta m_s = 2$  transition ESR signal for [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>] in dichloromethane.

is inhibited by the steric hindrance of the pyrrole  $\beta$ -mesityl group. In the solid, the parallel component of  $\Delta m_s = 1$  transition is separated into four lines due to the hyperfine structure of the copper nucleus and can be clearly observed near 1900 and 4400 G. Since the separation of the parallel signals corresponds to  $2D$ , a  $D$  value of  $0.1169 \text{ cm}^{-1}$  is obtained, which is almost identical to the value obtained from the  $\Delta m_s = 2$  transition signal.

To evaluate the intramolecular spin coupling of [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>], extensive variable-temperature (18–140 K) ESR measurements were made for [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>] in frozen dichloromethane. Below 18 K, ESR spectra of the triplet species were not obtained, which signifies a singlet ground state for [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>]. The temperature dependence of the  $\Delta m_s = 2$  transition signal of [Cu(TMTMP<sup>•+</sup>)] [SbCl<sub>6</sub>] is shown in Figure 4. As the temperature rises to 70 K, the signal increases, and over 70 K the hyperfine splitting of the signal broadens. The absorption peak area was calculated by double integration of the signal. The temperature dependence of the peak area of the  $\Delta m_s = 2$  transition signal is illustrated in Figure 5.

In order to explain the experimental result, the following Hamiltonian can be used

$$H = g\beta H(S_1 + S_2) - JS_1 \cdot S_2 + D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2) \quad (1)$$

where  $S_1$  is the spin of  $1/2$  on the copper,  $S_2$  is the spin of  $1/2$  on the porphyrin ligand, and  $D$  and  $E$  are the zero-field-splitting parameters of the copper ion. In our case,  $E$  can be neglected because of the axial symmetry of the complex.  $J$  is the exchange

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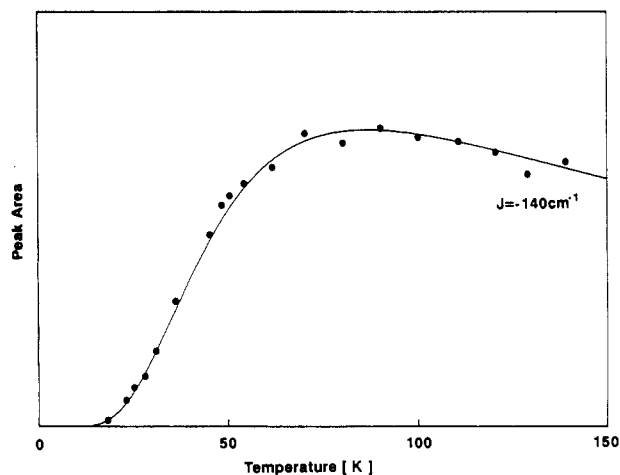


Figure 5. Temperature dependence of the peak area of the  $\Delta m_s = 2$  transition ESR signal and the calculated value (solid line) based on the spin Hamiltonian (eq 1).

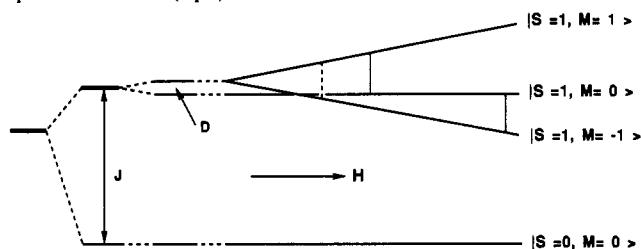


Figure 6. Energy states derived from the spin Hamiltonian (eq 1) in the case of antiferromagnetic coupling with a field applied in the  $z$  direction. The possible ESR transitions are indicated as a dashed line ( $\Delta m_s = 2$ ) and solid lines ( $\Delta m_s = 1$ ).

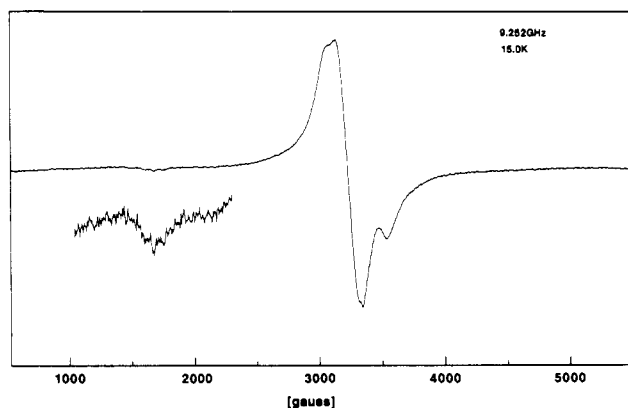


Figure 7. X-band ESR spectrum of  $[\text{Cu}(\text{TMP}^\bullet)][\text{SbCl}_6]$  in dichloromethane at 15 K.

interaction (spin coupling) between the copper spin and the porphyrin  $\pi$ -radical spin. To operate the eigenfunction, we can obtain the eigenvalues of the state, as shown in Figure 6. The temperature dependence of the peak area can be fitted by the parameters  $J = -140 \text{ cm}^{-1}$  and  $D = 0.1 \text{ cm}^{-1}$ .

Figure 7 shows the ESR spectrum of  $[\text{Cu}(\text{TMP}^\bullet)][\text{SbCl}_6]$  in frozen dichloromethane at 15 K. The features of the ESR spectrum are slightly different from that of  $[\text{Cu}(\text{TMTMP}^\bullet)][\text{SbCl}_6]$ . The signal at low field is much weaker than that of  $[\text{Cu}(\text{TMTMP}^\bullet)][\text{SbCl}_6]$ , which indicates a small  $D$  value for  $[\text{Cu}(\text{TMP}^\bullet)][\text{SbCl}_6]$ . The  $D$  value calculated from the position of the  $\Delta m_s = 2$  transition signal is  $0.018 \text{ cm}^{-1}$ . A pair of  $\Delta m_s = 1$  transition signals of  $[\text{Cu}(\text{TMP}^\bullet)][\text{SbCl}_6]$  are observed at 3050 and 3525 G, which overlap the signals of unoxidized copper(II) complexes. The temperature dependence of the signal seems to exhibit normal Curie law behavior.

**Magnetic Susceptibility.** The temperature dependence of the magnetic susceptibility of the microcrystal of  $[\text{Cu}(\text{TMTMP}^\bullet)]$

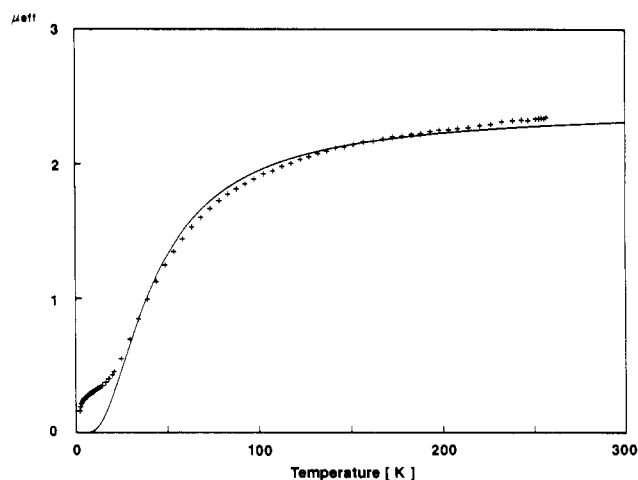


Figure 8. Magnetic susceptibility data for  $[\text{Cu}(\text{TMTMP}^\bullet)][\text{SbCl}_6]$  showing the agreement between the observed and calculated values. The solid line represents the simulation based on the spin Hamiltonian (eq 1).

$[\text{SbCl}_6]$  is shown in Figure 8 as a form of effective magnetic moment. The high-temperature (270 K) moment is  $2.35 \mu_B$ , which is slightly smaller than the spin-only value ( $2.45 \mu_B$ ) for an uncoupled system. The increase of  $\mu_{\text{eff}}$  as the temperature increases also indicates the  $S = 0$  ground state. The solid line in Figure 8 is a theoretical fit to the spin Hamiltonian (eq 1) with  $J = -120 \text{ cm}^{-1}$ . This places the  $S = 1$  state about  $120 \text{ cm}^{-1}$  above the  $S = 0$  ground state.

## Discussion

**Electronic Structure of  $[\text{Cu}(\text{TMTMP}^\bullet)][\text{SbCl}_6]$ .** Spectroscopic studies of monomeric  $\text{Cu}(\text{OEP})$  and  $\text{Cu}(\text{EtioP})$   $\pi$ -cation radicals were difficult due to the apparent aggregation of these species.<sup>10</sup> The ESR spectrum of the  $\text{Cu}(\text{OEP})$   $\pi$ -cation radical was characteristic of a dimeric copper(II) triplet state, which arose from the interaction of two copper centers and the spin-pairing of  $\pi$ -radical spin. Explanation of NMR signal positions for the  $\text{Cu}(\text{OEP})$   $\pi$ -cation radical was also complicated. The radical-induced shifts for ring methylene (1.4 ppm) and methyl residues (6.2 ppm) were surprisingly small, for an  $a_{1u}$  radical species.<sup>10</sup> Observation of the monomeric  $\text{Cu}(\text{OEP})$   $\pi$ -cation radical was made possible by  $\gamma$ -ray irradiation in a frozen tetrachloromethane matrix.<sup>13</sup> However, the present NMR and ESR spectra of  $[\text{Cu}(\text{TMTMP}^\bullet)][\text{SbCl}_6]$  clearly demonstrated the monomeric radical complex both in solution and in the solid state even at low temperature. The ESR spectrum of  $[\text{Cu}(\text{TMTMP}^\bullet)][\text{SbCl}_6]$  is identical to that produced by  $\gamma$ -ray irradiation of a frozen solution of  $\text{Cu}(\text{OEP})$  in that the low-field signal consists of a four-line component from the interaction of a single copper center. The large radical-induced NMR shift of  $[\text{Cu}(\text{TMTMP}^\bullet)][\text{SbCl}_6]$  also reveals the monomeric nature. Previously, Erler et al. succeeded in preparing monomeric  $\text{Cu}(\text{TMP})$   $\pi$ -cation radical by anticipating that the peripheral steric bulk of the *o*-methyl groups above and below the porphyrin plane would effectively isolate each metalloporphyrin molecule from even weak intermolecular interactions.<sup>8</sup> The steric effect of pyrrole  $\beta$ -mesityl groups would also isolate metalloporphyrin molecules, enabling the successful formation of monomeric  $[\text{Cu}(\text{TMTMP}^\bullet)][\text{SbCl}_6]$ .

Two types of metalloporphyrin  $\pi$ -cation radicals have been described, in which an  $a_{2u}$  radical exhibits large spin densities at the meso carbon and the pyrrole nitrogen, while the spin density of an  $a_{1u}$  radical is concentrated at the pyrrole carbon and has a node at the meso carbon.<sup>22</sup> Since the NMR isotropic shift of the meso deuterium is proportional to the meso carbon spin density,

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the typical  $a_{2u}$  radical is expected to induce an upfield contact shift of about 300 ppm for the meso deuterium.<sup>23</sup> Generation of the  $a_{1u}$  radical is expected to produce a small change in the isotropic shift.<sup>23</sup> The radical-induced shift of meso deuterium for [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> is 29 ppm, which is attributed to the  $a_{1u}$  radical state. The downfield shift of the pyrrole  $\beta$ -methyl proton signal is also consistent with the  $a_{1u}$  radical state.

It is worth noting that the zero-field parameter ( $D$  value) of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> is the same as that of the Cu(OEP)  $\pi$ -cation radical and much larger than that of [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>. Since a similar  $D$  value has been reported for the Cu(OEP) analogue,<sup>13</sup> which has  $D_{4h}$  molecular symmetry, we can rule out the possibility that the large  $D$  value for [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> arises from the decreasing molecular symmetry of TMTMP from  $D_{4h}$  to  $C_{4v}$ . Since [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> and the Cu(OEP)  $\pi$ -cation radical<sup>10</sup> possess the  $a_{1u}$  radical state and [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> has the  $a_{2u}$  radical state,<sup>8</sup> these differences would be due to the radical orbital occupancies of these radical species. The  $D$  value generally consists of the dipolar-dipolar interaction and the spin-orbital coupling. In this case, the dipolar-dipolar interaction would have the greater effect.

**Intramolecular Spin Coupling in Copper(II) Porphyrin  $\pi$ -Cation Radicals.** Since dimer formation is inhibited by the pyrrole  $\beta$ -mesityl group, as discussed in the preceding section, a clearer picture of the intramolecular spin coupling between copper(II) and its ligand radical for [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> should be possible.

Previously, Reed et al. proposed a theory based on the occupations and symmetries of the metal and ligand orbitals that contain unpaired electrons.<sup>6-8</sup> Making the reasonable assumption that site-isolated copper(II) porphyrin  $\pi$ -cation radical units will have local  $D_{4h}$  symmetry,<sup>24</sup> we see that the metal  $d_{x^2-y^2}$  orbital ( $b_{1g}$ ) is orthogonal to the  $a_{2u}$  orbital (HOMO of [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>). Therefore, the  $S = 1$  ground state can be derived according to Hund's rule, which leads to strong ferromagnetic coupling. This consideration is consistent with the ferromagnetic interaction of [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>.<sup>8</sup>

Even though the molecular symmetry of TMTMP decreases in  $C_{4v}$  due to different substitutions at pyrrole  $\beta$ -positions (i.e., methyl and mesityl), [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> would have orthogonal metal  $d_{x^2-y^2}$  ( $b_1$ ) and ligand  $a_{1u}$  ( $a_2$ ) magnetic orbitals and be expected to show an  $S = 1$  (i.e., triplet) ground state. However, the present temperature dependence of the ESR signal of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> in frozen dichloromethane clearly indicates the  $S = 0$  ground state. Simulation of the temperature dependence by the spin Hamiltonian (eq 1) indicates  $J = -140$  cm<sup>-1</sup>. Further, the solid-state magnetic susceptibility measurement of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> reveals antiferromagnetic coupling ( $J = -120$  cm<sup>-1</sup>) of copper(II) and porphyrin radical spins. This is in contrast with the very strong ferromagnetic coupling of [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>, whose exchange interaction ( $2J$  value) is more than +400 cm<sup>-1</sup>.<sup>8</sup>

The significant difference between the  $J$  values of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> and [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> may be due to the difference of the spin density at the pyrrole nitrogen atom: the  $a_{2u}$  radical has a large spin density, while the  $a_{1u}$  radical has

a node at this position. In a previous paper, we reported that the six-coordinated iron(III) OEP  $\pi$ -cation radical, which has an  $a_{1u}$  radical character, shows weak antiferromagnetic coupling ( $J \sim -5$  cm<sup>-1</sup>).<sup>14</sup> Since the  $a_{1u}$  orbital has a node at the pyrrole nitrogen atom, the coupling should be very small, which makes the spin in the radical orbital behave independently. Since [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> also has an  $a_{1u}$  radical character, we can expect weak spin interaction between the copper(II) and porphyrin radical spins of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>. Actually, the present ESR and magnetic susceptibility measurements show that the observed  $J$  value for [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> is much smaller than that for [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>. [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> does not have ideal  $C_{4v}$  symmetry, as expected from the  $D$  value. The radical orbital mixes slightly with the  $d$  metal orbital, and the coupling becomes antiferromagnetic. The negative spin density at the pyrrole nitrogen atom is also related to the antiferromagnetic coupling of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>. Since the deuterium NMR spectrum of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> reveals negative spin density at the meso carbon, which is a node in the  $a_{1u}$  orbital, it is reasonable to assume a negative spin density at the pyrrole nitrogen, which is also a node in the  $a_{1u}$  orbital. The exchange interaction between copper(II) spin and negative spin at the pyrrole nitrogen atom stabilizes the antiferromagnetic state.

It is worth noting that the  $J$  value of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> is larger than that of the previous six-coordinated OEP  $\pi$ -cation radical.<sup>14</sup> As discussed above section, the  $D$  value of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> is also larger than those of the six-coordinated iron(III) OEP  $\pi$ -cation radical<sup>14</sup> and [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>. Since the  $D$  value reflects the symmetry around metal, the large  $D$  value of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub> would suggest the slight deviation from the strict planar structures which were observed for the iron(III) OEP  $\pi$ -cation radical and [Cu(TMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>.<sup>8,15</sup> Reed et al. indicated that the antiferromagnetic interaction would be strong in the ruffled porphyrin. Thus, the large  $D$  value also may be related to the large negative  $J$  value of [Cu(TMTMP<sup>•</sup>)]<sub>6</sub>SbCl<sub>6</sub>.

As shown in the present study, a strong triplet ESR signal is observed at moderate temperature with antiferromagnetic coupling. However, in ferromagnetic coupling, a strong ESR signal is observed at low temperature. Since the strong triplet ESR spectrum for the Cu(OEP)  $\pi$ -cation radical has been observed at liquid-nitrogen temperature (77 K),<sup>13</sup> it is reasonable to expect antiferromagnetic coupling in the Cu(OEP)  $\pi$ -cation radical species. This is consistent with the present suggestion, which predicts antiferromagnetic coupling for the  $a_{1u}$  occupancy of the Cu(OEP)  $\pi$ -cation radical.

While recent studies of iron(III) OEP  $\pi$ -cation radicals have focused on the relative magnitudes of the coupling of metal spins with the  $a_{1u}$  and  $a_{2u}$  radicals, the present study shows weak antiferromagnetic coupling between metal spin and  $a_{1u}$  radical spin. This may be due to the spin distribution of the  $a_{1u}$  orbital, which has a node or a negative spin density at the pyrrole nitrogen atom.

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