Simulation of Temperature-Dependent EPR Spectra of Mixed-Valence Copper(II)-Copper(I) Complexes

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Temperature-dependent, solution EPR spectra of two mixed-valence copper(II)-copper(I) complexes have been simulated by using modified Bloch equations. The transition probability for the intramolecular electron transfer is determined from the simulation. The transition probabilities have been fitted to the Arrhenius equation to derive the activation energies. The transition probablity also varies according to the solvent used.

Introduction

Mixed-valence binuclear $Cu^{II}Cu^{I}$ complexes are of importance in the study of intramolecular electron transfer[1] and they may serve as a model of the mixed-valence state detected for binuclear copper sites in cuproproteins[2]. Some mixed-valence $Cu^{II}Cu^{I}$ complexes show four-line EPR spectra[3], indicating that the unpaired electron is trapped on one copper ($I = 3/2$) ion[4]. But several complexes show temperature-dependent seven-line EPR spectra, indicating that the unpaired electron is hopping between the two copper ions. Gagné et al. reported such a complex (Complex G) in 1979[5], and Hendrickson's group reported four more related complexes (Complexes I, II, III, and V) in 1983[6]. Their structures are illustrated below.
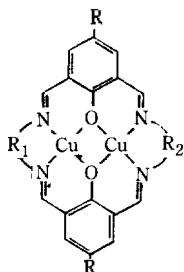
G.   R = methyl, $R_1 = R_2$ = propylene
I.   R = *tert*-butyl, $R_1 = R_2$ = propylene
II.   R = *tert*-butyl, $R_1 = R_2$ = 2,2'-dimethylpropylene
III.   R = *tert*-butyl, $R_1 = R_2$ = butylene
V.   R = *tert*-butyl, R_1 = propylene,
      R_2 = 2,2'-dimethylpropylene

Simulation of the temperature-dependent spectra of these complexes has not been reported. In fact, Hendrickson's paper states that "it is a near to impossible task at best to simulate these solution state spectra." In this paper we show that the solution EPR spectra of Complexes G and III can be simulated reasonably by using the modified Bloch equations which have originally been derived to describe the NMR line shape for a jumping spin[7,8]. Simulation of the spectra has made it possible to determine the transition probabilities and activation energies for the intramolecular electron transfer in these complexes.

Simulation of the Spectra

Here we consider only those complexes in which the two copper ions are equivalent. Our general approach is to cal-

culate the positions of four hyperfine lines[4] expected when the unpaired electron is trapped on one copper ion, then calculate the spectrum for each combination of two nuclear spin states using the modified Bloch equations, and finally add up the spectra for all possible combinations of the nuclear spin states.

When the unpaired electron is trapped on one copper ion, the positions of the hyperfine lines in the solution spectrum may be calculated by the following equation[9]:

$$B(m) = \frac{1}{g\beta}\left[h\nu - am - \frac{a^2}{2h\nu}\{I(I+1) - m^2\}\right] \tag{1}$$

where m is $-I, -I+1, \ldots, +I$, and g and a are the g value and the hyperfine coupling constant. When an electron is hopping between two equivalent copper atoms, Cu_A and Cu_B, the total complex magnetic moment is given by the following equation[10]:

$$\hat{M} = -\gamma B_1 M_o \frac{0.5(2\omega - \hat{\omega}_A - \hat{\omega}_B) + 2iP}{\{(\omega - \hat{\omega}_A) + iP\}\{(\omega - \hat{\omega}_B) + iP\} + P^2} \tag{2}$$

$$\hat{\omega}_A = \omega_A - i/T_{2A} \tag{3}$$

$$\hat{\omega}_B = \omega_B - i/T_{2B} \tag{4}$$

where P is the transition probability of the electron from one copper atom to the other in the unit time, T_{2A} and T_{2B} are the transverse relaxation times of the electron in Cu_A and Cu_B, M_o is the static magnetization, ω_A and ω_B are the resonance frequencies $\times 2\pi$ at two copper atoms in the absence of hopping, and other symbols have their usual meaning.

The intensity of the spectral line is proportional to v, the imaginary part of $\hat{M}$. In order to express v as a function of the magnetic field, we introduce the following relations:

$$\omega - \omega_A = g\beta\hbar^{-1}(B - B_A), \quad \omega - \omega_B = g\beta\hbar^{-1}(B - B_B) \tag{5}$$

$$W_A = \hbar/g\beta T_{2A}, \quad W_B = \hbar/g\beta T_{2B} \tag{6}$$

$$P' = P/g\beta\hbar^{-1} \tag{7}$$

where W_A and W_B represent the line width parameters and P' the transition probability in the gauss unit. Then $\hat{M}$ and v can be expressed as

$$\hat{M} = \frac{-\gamma B_1 M_o \hbar}{g\beta} \times \frac{S + Ti}{Q + Ri} \tag{8}$$
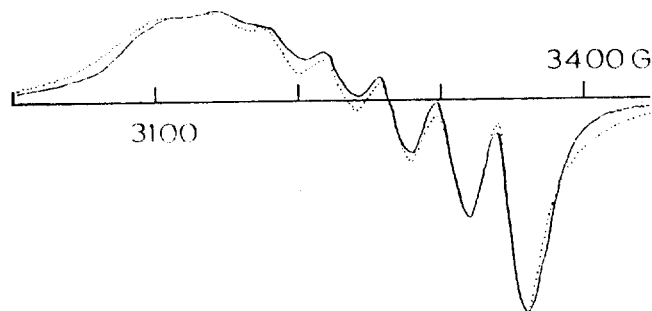
Figure 1. Measured (———) and simulated (· · · ·) EPR spectra of Complex III in toluene–acetone at 298K. Parameters used in simulation are listed in Table 1. Measured spectrum is from ref. 6.

$$v = \frac{-\gamma B_1 M_s \hbar}{g\beta} \times \frac{QT - SR}{Q^2 + R^2} \tag{9}$$

$$Q = (B - B_A)(B - B_B) - W_A W_B - P'(W_A + W_B)/2\pi \tag{10}$$

$$R = (B - B_A)(W_B + P'/2\pi) + (B - B_B)(W_A + P'/2\pi) \tag{11}$$

$$S = 0.5(2B - B_A - B_B) \tag{12}$$

$$T = 0.5(W_A + W_B) + P'/\pi \tag{13}$$

The first derivative of v with respect to the magnetic field B is given by

$$\frac{dv}{dB} = -\frac{\gamma B_1 M_0 \hbar}{g\beta}$$

$$\times \frac{(Q'T + R'S)(Q^2 + R^2) - 2QT - RS)(QQ' + RR')}{(Q^2 + R^2)^2} \tag{14}$$

$$Q' = 2B - B_A - B_B \tag{15}$$

$$R' = W_A + W_B + P/\pi. \tag{16}$$

The line width is known to vary according to the formula[11]

$$W = c + dm + fm^2. \tag{17}$$

Since there are only four hyperfine states for the copper ion, i.e., one more than the number of adjustable parameters in Eq. (17), all four values of W have been considered as independently adjustable parameters.

Thus we have used seven adjustable parameters: g, a, P', and four line width parameters. g and a determine the line positions, P' determines the relative intensities of the seven hyperfine lines, and the line width parameters determine the line widths or the peak heights of the hyperfine lines.

The spectra have been calculated by using a personal computer.

Results

Complex III. The Hendrickson's paper presented a room temperature spectrum of Complex III in toluene–acetone and a series of temperature-dependent spectra of the same complex in acetone. The simulated spectrum is compared with
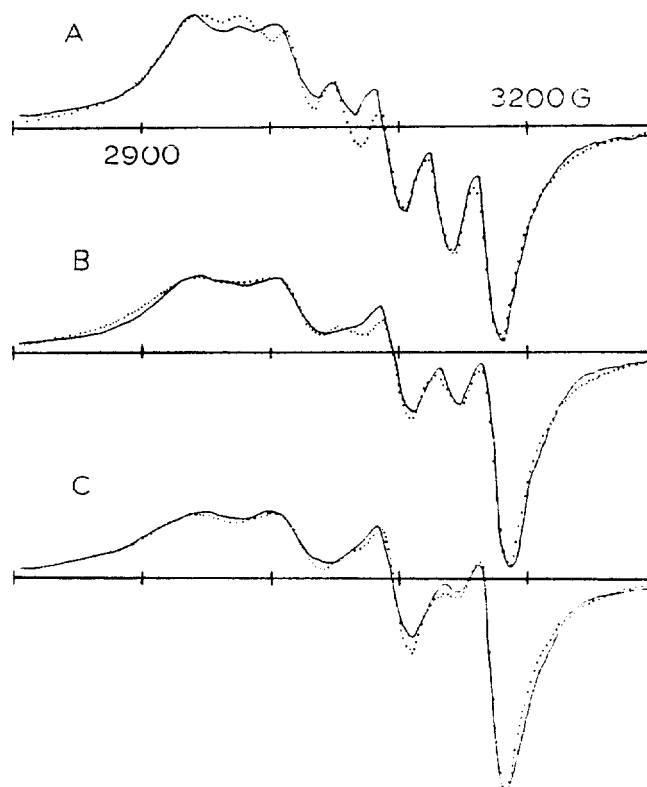

Figure 2. Measured (———) and simulated (· · · ·) EPR spectra of Complex III in acetone at (A) 306K, (B) 275K, and (C) 261K. Parameters used in simulation are listed in Table 1. Measured spectra are from ref. 6.

Table 1. Parameters used for simulating the EPR spectra of Complex III.

Solvent	Temp.(K)	g	a(cm^{-1})	W(G)*	P'(G)	$P(10^9$ s^{-1})
toluene–acetone	298	2.112	0.0078	46, 32, 26, 20	628	1.85
acetone	306	#	0.0070	38, 26, 23, 21	515	1.51
acetone	275	#	0.0073	50, 32, 24, 20	314	0.92
acetone	261	#	0.0072	50, 32, 22, 18	239	0.72

* The line widths of the four hyperfine lines in the order of increasing magnetic field. # The g value could not be determined because the microwave frequency was not given in ref 6; $g = 2.1$ was assumed.

the measured room temperature spectrum in Figure 1. The overall fit is quite good. The resulting transition probability is 1.85×10^9 s^{-1} (628G).

The spectra of the complex in acetone at 306, 275, and 261K, which show features characteristic of electron hopping, have also been simulated, and the results are shown in Figure 2. The simulation for the 306K spectrum is not very satisfactory: the low-field side of the calculated spectrum does not match very well the measured spectrum. Since the intensity of the sixth peak is most sensitive to the P' value, the spectrum has been simulated so that the high-field side matches the measured spectrum. The resulting transition probabilities are 1.51×10^9 at 306K, 0.92×10^9 at 275K, and 0.72×10^9 s^{-1} at 261K. The parameters used in the simulation are listed in Table 1.

Simulation of EPR Spectra of Mixed-Valence CuII CuI Complexes

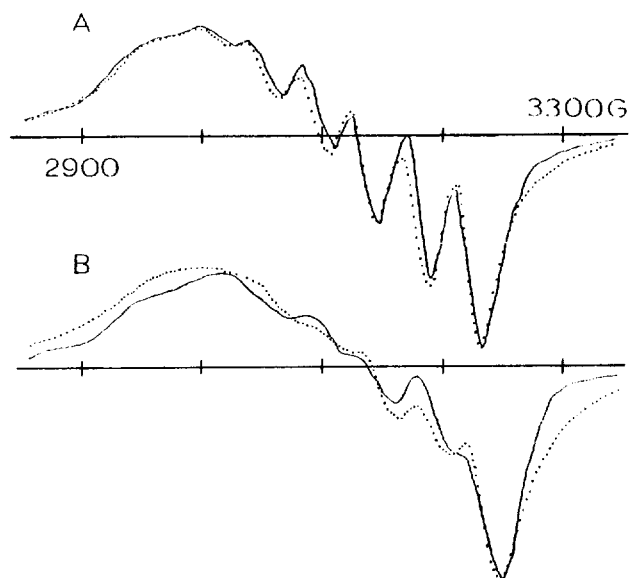*Bull. Korean Chem. Soc., Vol. 8, No. 2. 1987* 113

Figure 3. Measured (——) and simulated (· · · ·) EPR spectra of Complex G in CH_2Cl_2-toluene at (A) 280K and (B) 250K. Parameters used in simulation are listed in Table 2. Measured spectra are from ref. 5.

Table 2. Parameters used for Simulating the EPR Spectra of Complex G

Solvent	Temp.(K)	g	a(cm⁻¹)	W(G)*	P'(G)	P(10⁹ s⁻¹)
CH_2Cl_2–toluene	280	#	0.0085	50, 30, 26, 23	820	2.5
CH_2Cl_2–toluene	250	#	0.0085	65, 45, 35, 29	470	1.4
CH_2Cl_2	ambient	2.169†	0.0089	41, 33, 28, 23	20000	61

* The line widths of the four hyperfine lines in the order of the increasing magnetic field. # The g value could not be determined because the microwave frequency was not given in ref. 5; g=2.169 was assumed. † Ref. 4.

Complex G. The two spectra at 280 and 250K, which show features characteristic of electron hopping, have been simulated, and the results are shown in Figure 3. The 250K spectrum is quite broad and the simulation is not very satisfactory. But simulation of the high-field side was possible only for a narrow range of the P'-value. The resulting transition probabilities are 2.5×10^9 at 280K and 1.4×10^9 s⁻¹ at 250K. The parameters used in the simulation are listed in Table 2.

Gagné et al. also presented an ambient temperature spectrum of Complex G dissolved in methylene chloride under helium atmosphere[5]. A satisfactory simulation of this spectrum could be obtained for a very large value of P; see Figure 4 and Table 2.

Discussion

Simulation of the Spectra. We have shown that the temperature-dependent EPR spectra of Complexes G and III, in which the two copper ions are equivalent, can be simulated reasonably. The spectra of Complex I, another complex with two equivalent copper ions, could not be simulated satisfactorily. It is interesting to note that its spectra are rather similar
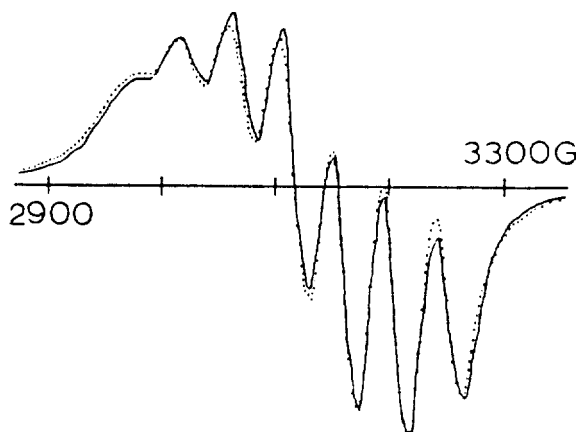

Figure 4. Measured (——) and simulated (· · · ·) EPR spectra of Complex G in CH_2Cl_2 at ambient temperature. Parameters used in simulation are listed in Table 2. Measured spectrum is from ref. 5.

to those of Complex V which has two inequivalent copper ions. When the two copper ions are not equivalent, they may have two different values for each parameter. We have found simulation of these spectra more difficult because of the large number of adjustable parameters. The spectrum of Complex II was not simulated, because the measured spectrum was not available.

Spectral change is very sensitive to the P' value when it is less than about 1500G, corresponding to the transition probability which makes the two outermost hyperfine lines coalesce. When P' is greater than this value, the spectral change is less sensitive to the P' value. Thus P'=20,000G for the ambient temperature spectrum of Complex G is less accurate.

Solvent Effects. It is noted that the transition probability is dependent on the solvent. Complex III in toluene–acetone shows a larger transition probability than the same complex in acetone at the same temperature. The solvent effect is more striking for Complex G: the transition probability for the complex in CH_2Cl_2 is more than 20 times that of the complex in CH_2Cl_2–toluene.

Gagné et al. found that the electron was trapped on one copper atom at room temperature when Complex G was dissolved in CH_2Cl_2 under CO atmosphere. It seems that coordination of CO to an axial site of a copper ion is responsible for the localization of the electron. Some solvent molecules including $CHCl_3$ are known to coordinate axially to square planar copper complexes[12] and CH_2Cl_2 and acetone are likely to behave in a similar fashion. If a solvent molecule coordinates to a copper ion, it is expected to change the transition probability.

The second solvent effect is the spectral change, which makes the spectrum deviate from the simulated spectrum. The measured spectrum of Complex III in toluene–acetone matches the simulated spectrum closely, while that of Complex III in acetone at 306K and that of Complex I do not match the simulated spectra very well. The complexity of the spectrum may originate from (1) the nonequivalence of the two copper ions caused by preferential ligation of the solvent molecule to either Cu^I or Cu^{II} and/or (2) coexistence of two EPR-active species, one with a coordinated solvent molecule and the other without a coordinated solvent molecule.
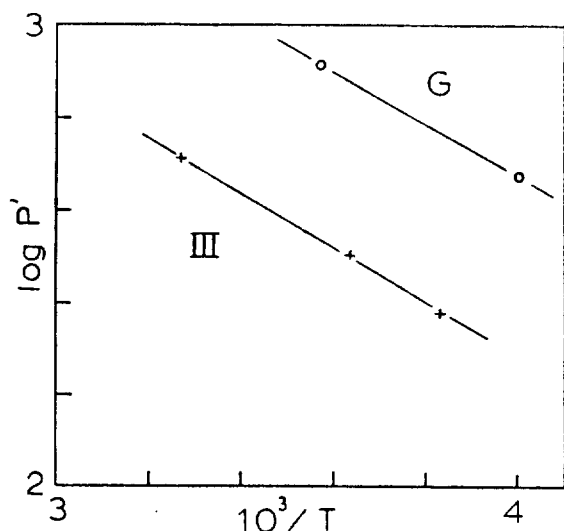
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Figure 5. Temperature dependence of the transition probabilities of the intramolecular electron transfer for Complex G and Complex III. The resulting activation energy is 2.6 kcal/mol for both cases.

Activation Energy. The P' values for Complex III in acetone can be fitted to the Arrhenius equation

$$P' = A \exp(-E/RT). \tag{18}$$

The resulting activation energy and pre-exponential factor are $E = 2.6$ kcal/mol and $A = 1.1 \times 10^{11}$ s^{-1} (see Figure 5). Although only two P' values are available for Complex G in CH_2Cl_2-toluene, fitting of these values to the Arrhenius equation gives $E = 2.6$ kcal/mol and $A = 2.6 \times 10^{11}$ s^{-1}.

It is generally accepted that the thermal electron exchange is preceded by geometrical adjustments to equalize the environments of both metal sites[13]. For the complexes studied here, it was suggested a structure intermediate between square planar for Cu^{II} and square planar with slight tetrahedral distortion for Cu^{I} might be involved. If we assume that this structure is attained by a particular vibrational state whose energy is $E = 2.6$ kcal/mol (910 cm^{-1}), then the transition probability is expected to be proportional to the number of molecules in this vibrational state and the frequency[14] of this vibration ν

$$P = k\nu \exp(-E/RT). \tag{19}$$

Here k is a factor representing the fraction of the vibration accompanied by the electron transfer.

Complex III in acetone and Complex G in CH_2Cl_2-toluene have the same activation energy for the intramolecular electron transfer, indicating that the energy of the vibrational state involved is not affected by the structural difference in these two complexes. Their k values are 0.004 for Complex III and 0.01 for Complex G. The reason for the difference in the k

values is not understood yet.

Concluding Remarks

To our knowledge this work is the first successful simulation of solution EPR spectra of mixed-valence transition metal complexes. We believe this work can be extended to mixed-valence systems with inequivalent metal ions[15], and also to polycrystalline EPR spectra of mixed-valence Cu(II)-Cu(I)[2] and V(IV)-V(V) systems[16]. Further work is needed to clarify the solvent effects on the spectrum and the transition probability.

References and Notes

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