

Effects of UV Irradiation on ESR and Optical Properties of Cu(II) Ions in Organic Solid Solutions Containing CuCl at 77 K

Y.M. Hase^{*1}, Y. Nakano² and T. Saito²

¹Department of Mechanical Science and Bioengineering, Osaka University, Toyonaka, Osaka 560-8531, Japan;

²Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-0494, Japan

Abstract: The effect of uv irradiation on the solid solutions of MTHF and EtOH containing CuCl with HCl has been investigated. The axial ESR spectra observed before uv irradiation at 73 K for these solutions indicate that Cu(II) ions exist in such a way that the unpaired electron density locates on $3d^9$ orbital in the coordination structure associated with the ligand molecules. The new ESR signals observed after uv irradiation is inferred to Cu(II) ions of a transformed ligand structure that is formed *via* an exciplex “adiabatically”. We infer that the new species induced by uv irradiation forms strong covalent bonds between Cu(II) ions and the ligand. The formation of the exciplex has also been evidenced by the absorption and emission properties for the same solutions at 77 K. Three types of emissive exciplexes have been proposed.

INTRODUCTION

Copper ions and/or atoms as biologically essential substances have important roles such as oxygen carrier and charge transfer reactions. Especially, the effects of the structural changes due to ligand atoms on the electrical redox potential of Cu(I)/Cu(II) have been studied experimentally and theoretically in inorganic and bioinorganic fields. Recently, there grows the strong concern in the long-range charge transfer between metal centers in a variety of research fields as well as the biological field [1-3].

As a fundamental research to elucidate the function and effects of metal ions and/or atoms in biological systems, we have been investigating the ESR and optical properties of 1B metal atoms produced radiation-chemically by reducing their mono cations in solid solutions [4-12]. In the series of our previous studies, formation of metal atoms, Cu^0 , Ag^0 and Au^0 in γ irradiated solid solutions containing their mono cations were evidenced by ESR spectra that exhibited duplicate quartets [10], duplicate doublets [8] and quartet [12], respectively. The values of the hyperfine splitting, a and the gyromagnetic ratio for the electron shell, g_J were evaluated from the Breit-Rabi equations that were applied for the case of isotropic forces of interaction between trapped atoms and ligands. According to the relative shift of the values of a and g_J for those of free Cu^0 atoms, we showed that the delocalization of the unpaired spin density of Cu^0 atoms onto ligands is the largest of the three. We also proved experimentally that an admixture of the wave function of the Cu^0 atom in its ground state $2S_{1/2}; 3d^{10}4s^1$ into $3d_{x^2-y^2}$ is expected to occur to some extent. The five uv absorption bands represented as bands from C_1 to C_5 were observed after γ irradiation in the organic solid solutions at 77K [10]. We attributed them to the two types of exciplexes formed between excited Cu^0

atoms and the ligands: one associates with Cu^+ ions as well as solvent molecules, the other consists mainly of solvent molecules. We also showed that the emission band at 520 nm that was induced by 250 nm (C_7 band) excitation before irradiation was reduced in the intensity after γ irradiation and that this is as a consequence of conversion of Cu^+ ions to Cu^0 atoms. It was inferred previously that the emission at 520 nm observed before irradiation was due to the exciplex formed by excitation at 250 nm (C_7 band). The results have motivated us to further investigate the effect of uv irradiation on the same solid solutions at 77 K so that we have used UVB and UVC lamps with the peak wavelengths at 310 nm and at 253.7 nm, respectively, that emit the lights of the wavelengths close to absorption bands C_6 and C_7 , respectively. We have observed that the colors of the samples have been changed after uv irradiation. This fact has led us to infer the formation of a new exciplex.

In order to obtain further information on the dynamical changes of the ligand structure around the central metal ions caused by uv and γ irradiation and to elucidate the formation mechanism and stabilization of exciplexes produced by uv and γ irradiation, the present ESR and optical studies have been carried out for 2-methyltetrahydrofuran (MTHF) and ethanol (EtOH) solid solutions with HCl containing CuCl.

EXPERIMENTAL

Reagent grade CuCl of stated purity of 99.9% and reagent grade EtOH were purchased from Wako Pure Chemicals Industries, Ltd. and used as supplied. Reagent grade MTHF was distilled fractionally so that no optical absorption due to its chemical additives was observed in the wavelength region longer than 230 nm. The amount of 10 ml of both MTHF and EtOH solvents was first bubbled by N_2 gas sufficiently to remove oxygen gas in the solvents. CuCl was then added under N_2 bubbling and stirring the solvents. The solute was completely dissolved in the solvents after adding hydrochloric acid (35% in content) of 0.2 ml for the concentrated solutions of 10^{-1} M. The color of MTHF solutions at room

*Address correspondence to this author at the Department of Mechanical Science and Bioengineering, Osaka University, Toyonaka, Osaka 560-8531, Japan; Tel: +81 06 6850 6192; Fax: +81 06 6850 6212; E-mail: miyatake@me.es.osaka-u.ac.jp

temperature was yellow and deepened with increasing the concentration of CuCl, while EtOH solutions showed almost transparent for a dilute solution of 10^{-3} M, coloring yellowish-green for 10^{-1} M. The fresh solutions were transferred into ESR tubes of 4mm inner diameter for ESR, emission and excitation measurements and optical cells of 1mm light path length for optical absorption measurements. ESR tubes and optical cells were previously filled with N_2 gas to remove air, and the tubes filled with solutions were then immersed into liquid nitrogen. The color of solutions was faded away at liquid nitrogen temperature, except for the MTHF solution of 10^{-1} M, which colored slightly yellow. The procedures of sample preparation were the same as in our previous studies [10]. The effect of evacuation of the samples by freeze-pump-thaw method as well as sealing the sample tubes was not observed on the ESR spectral characteristics. In order to investigate the ESR and optical properties for the samples of the solid solutions containing Cu(I) and Cu(II) under the same conditions, we have used the same CuCl systems as in the previous study[10]: EtOH as the polar solvent and MTHF as less polar solvent were used to investigate dependence of polarity on the spectral characteristics.

UV irradiation was carried out at 77 K with use of two kinds of lamps of Philips NIPPON P/I CO., LTD.: one was TL12 emitted light of the UVB region and the other was TUV emitted the monochromatic light of 253.7 nm (UVC region). The former provides maximum intensity at 310 nm with a half-height width of about 40 nm. A typical dose was $1.2\text{--}1.5$ J/cm². γ irradiation was carried out at 77 K for the uv irradiated samples. The total dose was 23 kGy. After γ irradiation, the samples were illuminated with the light of wavelength longer than 600 nm to bleach trapped electrons.

X band ESR measurements were carried out with use of a JEOL spectrometer of 100 kHz modulations at 73 K by bubbling helium gas in liquid nitrogen of an ESR Dewar to

avoid bubbling of N_2 gas. The calibration of g -value was carried out with an Mn^{2+} standard sample that was immersed in the Dewar together with the irradiated samples. The experimental apparatus and procedures for the optical absorption measurements at 77 K were described elsewhere [4, 5]. The measurements of the emission and excitation spectra were carried out at 77 K with use of a Hitachi fluorescence spectrometer (model F-4500) for the same samples subsequently after ESR measurements. Color filters, for example, UV29, L39, Y44, Y46, were used for the removal of scattered excitation light in the measurements.

RESULTS AND DISCUSSION

ESR Properties

The X band ESR spectra observed at 73 K before, after UVB and successive after γ irradiation for MTHF and EtOH solutions with HCl dissolving 10^{-1} M CuCl are shown in Figs. (1A and B), respectively.

In the ESR spectra obtained before uv irradiation in the present study shown as (a) in Figs. (1A and B), the characteristic set of the ESR signals consisting of four lines as well as a structureless, broad line were observed at 77 K in the magnetic field region of 260 – 340 mT. These ESR spectra in our system are quite similar to those due to paramagnetic Cu(II) ions subjected to axial crystal field, which have been reported previously by many researchers in a variety of research fields as well as the biological field [13-23]. The spectra have been attributed to well resolved parallel and unresolved perpendicular components of the hyperfine splitting due to the Cu(II) ions with unpaired electron on $3d^9$ in ground state that are subjected to an axial crystal field.

In the ESR spectra observed after UVB irradiation shown as (b) in Figs. (1A and B), we have observed, for the first time, the spectra that are different from those before UVB

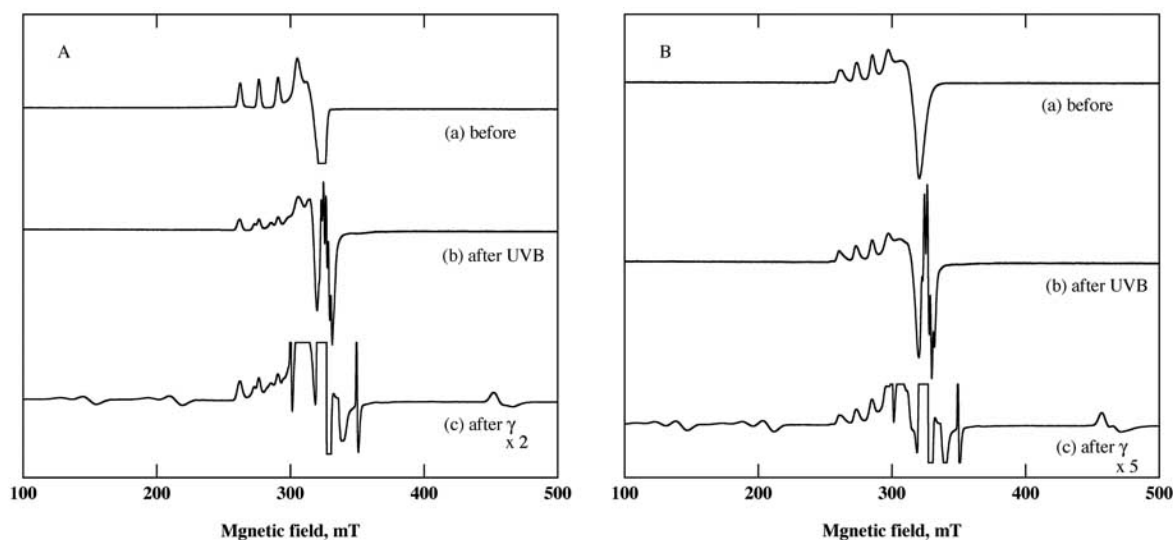


Fig. (1). X band ESR spectra observed at 73 K for the solid solutions of MTHF (A) and EtOH (B) containing 10^{-1} M CuCl with 0.2 ml HCl per solvent of 10 ml, which are obtained before (a), after uv irradiation (b) and after subsequent γ irradiation (c), respectively. UV irradiation was carried out at 77 K by using the UVB lamp that provides the light of maximum intensity at 310 nm with a half-height width of about 40 nm. The maximum total dose for the uv irradiation was typically 1.2 J/cm². γ irradiation was carried out at 77 K subsequently for the uv irradiated samples. Typical γ dose was 23 kGy. Two sharp ESR lines observed at 300 mT and 350 mT for both cases are due to H atoms that were produced and trapped in a Suprasil quartz tube by γ irradiation. The relative receiver gain for (A) to (B) was 1 : 50.

irradiation. We will mention this later in detail. The ESR spectra obtained after γ irradiation in the present study subsequent to uv irradiation were the same as those reported previously [10]. As shown in spectra (c) in Figs. (1A and B), they exhibit the duplicate hyperfine quartets consisting of three groups; first, two resolved pairs of lines at about 140 and 210 mT, second, two lines appearing on the edge of the large signal due to solvent radical at about 330 mT and third, a poorly resolved doublet line appearing at about 470 mT. We have ascribed the spectra to Cu^0 atoms that were produced by reduction of Cu^+ ions with electrons generated in γ -irradiated solid solutions at 77 K [10]. We confirm that Cu^0 is also produced by γ irradiation in this study.

The expanded ESR spectra observed before and after uv irradiation in the magnetic region of 250–360 mT at 73 K for

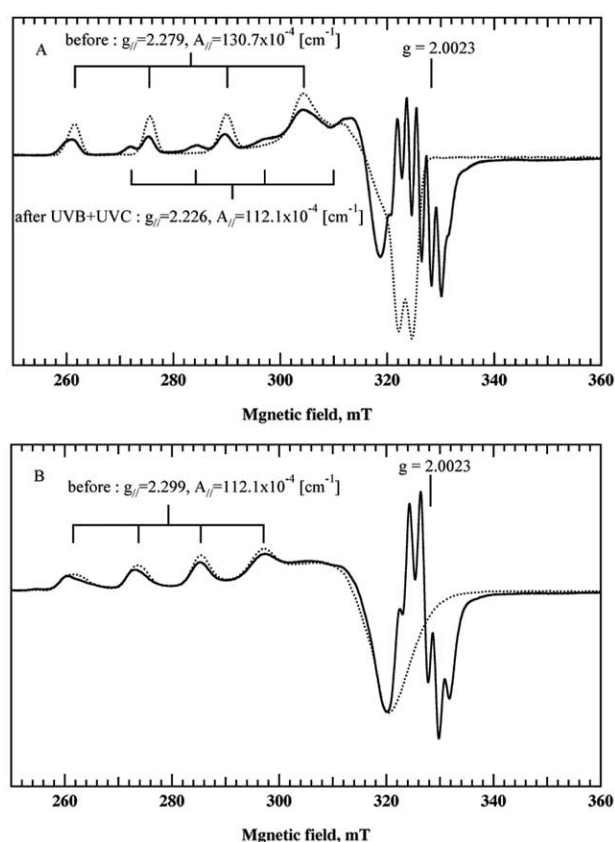


Fig. (2). ESR spectra observed at 73 K for solid solutions of MTHF (A) and EtOH (B) containing 10^{-3} M and 10^{-1} M CuCl with 0.2 ml HCl per solvent of 10 ml, respectively. The microwave frequency of 9.185 GHz and 9.194 GHz were used for MTHF and EtOH solution, respectively. The dotted and solid lines represent the ESR spectra obtained before and after uv irradiation, respectively. UV irradiation was carried out at 77 K by using the UVB and UVC lamps for the solid solution of MTHF (A), and the UVB lamp for the solid solution of EtOH (B). UVB lamp provides the light that has maximum intensity at 310 nm with a half-height width of about 40 nm. UVC lamp emits monochromatic light of 253.7 nm. The maximum total dose for uv irradiation was typically 1.2 J/cm^2 .

MTHF and EtOH solutions with HCl dissolving 10^{-3} M and 10^{-1} M CuCl are shown in Figs. (2A and B), respectively. The ESR spectral profiles and parameters for 10^{-3} M solutions were identical to those for 10^{-1} M solutions, although the former spectra reduced in the intensity.

The present spectra obtained before uv irradiation, representing as dotted lines in Figs. (2A and B), have already been identified as follows [13]. The four satellites that are equally spaced and well resolved in the magnetic field region of 260 – 300 mT are due to $g_{||}$ components of Cu(II) ion in an axial crystal field. The unresolved, broad line centered at around 320 mT is due to g_{\perp} component. Thus the spectra observed in this study indicate that Cu(II) ion is formed in MTHF and EtOH solutions under the presence of hydrochloride. It is known that in normal conditions, CuCl is an unstable compound. In fact, the color of the solutions has been changing during storage at room temperature. For 10^{-1} M CuCl/MTHF+HCl solution, the color turned dark brown, while 10^{-1} M CuCl/EtOH+HCl solution showed dark yellowish-green after storage for 2 hours at room temperature. These colors are known to be characteristic of the CuO precipitate [16] and the solution of tetrachloro-Cu(II) complex ions [18], respectively. The ESR spectra obtained at 73 K for the samples stored at room temperature more than 24 hours increased in the intensities by more than 20 times without any spectral change. This result shows another evidence that Cu(II) ion is formed in the solutions used in this study. We infer that Cu(II) ion with unpaired electron density on $3d^9$ orbital locates in a coordination field of the ligand molecules, showing the axial ESR spectra. In this context, we refer the ligand as solvent molecules. However, we cannot deny the possibility that the counter ion, Cl^- locates in the vicinity of Cu(II) ions. The g -values shows $g_{||} > g_{\perp} > 2.0023$, indicating that the ground state of the central Cu(II) ions is $d_{x^2-y^2}$ with a square planer configuration.

After uv irradiation, the color of the samples turned deep orange for both MTHF and EtOH solutions. Irradiation by the lamp that emits light of UVC region subsequent to irradiation by light of UVB region caused no prominent change in the ESR spectra due to Cu(II) ion. The ESR spectrum obtained at 73 K after uv irradiation for MTHF solutions, representing as solid line in Fig. (2A), showed a new set of four lines on the high-field side of the four lines observed before uv irradiation in the region of 260–320 mT. The appearance of the new set observed after irradiation is accompanied by a decrease in the intensity of the previous set observed before irradiation. For EtOH solutions as shown in Fig. (2B), the corresponding ESR lines were not observed after uv irradiation, but each line observed before uv irradiation slightly broadened and declined to high-field side, indicating a superposition of new lines. The ESR spectra after uv irradiation also showed the resolved structures in the field region of 320–334 mT. These are attributed to well-known solvent radicals. This will be discussed later. The values of $g_{||}$ and $A_{||}$ after uv irradiation are smaller than those before uv irradiation for the case of MTHF solutions, indicating that the structure of central Cu(II) ion is transformed from square planer into tetrahedral configuration. The ESR parameters obtained in the present study are summarized in Table 1.

Table 1. The ESR Parameters Obtained for the Solid Solutions Containing CuCl at 73 K

Solvent (+HCl)		ESR parameters ^a		
		$g_{//}$	g_{\perp}	$A_{//} \times 10^{-4} \text{ cm}^{-1}$
MTHF	before	2.279	$(2.03 \pm 0.05)^b$	130.7
	after uv	2.226	2.012 ± 0.012	112.1
EtOH	before	2.297	$(2.03 \pm 0.05)^b$	112.1
	after uv	$(2.297)^c$	2.006 ± 0.012	$(112.1)^c$

^aThe parallel components, $g_{//}$ and $A_{//}$, were determined by calibrating with Mn^{2+} signals, since the four lines observed at 73 K were almost equally spaced and well resolved.

^bThe perpendicular components must lie in the magnetic region of 312 – 328 mT so that the value of g_{\perp} is estimated to be 2.03 ± 0.05 for both solid solutions observed before irradiation at 73 K.

^cThe four signals observed after UVB irradiation for 10^{-1} M CuCl/EtOH + HCl solid solutions were almost the same as those observed before irradiation.

The ESR parameters, $g_{//}$, g_{\perp} and $A_{//}$, enable one to estimate a degree of the delocalization of the unpaired electron in a crystal field. According to the equation derived by Kivelson and Neiman [24] for electrons occupying a B_{1g} orbital of a Cu(II) complex, the measure of the delocalization of the unpaired electron, α^2 , can be estimated by $\alpha^2 = A/P + (g_{//} - 2) + 3(g_{\perp} - 2)/7 + 0.04$ [13, 20]. In the present case before irradiation, the parallel components $g_{//}$ and $A_{//}$ were well determined, since the four lines were almost equally spaced and well resolved at 73 K. It is difficult to determine precisely the perpendicular component, g_{\perp} , because of the absence of the hyperfine structure. However, the perpendicular component must lie in the magnetic region of 312 – 328 mT. This leads us to infer that the value of g_{\perp} is estimated to be 2.03 ± 0.05 for both solid solutions observed at 73 K before irradiation. With use of the estimated value of g_{\perp} , the values of α^2 are 0.76 and 0.64 for MTHF solid solutions before and after uv irradiation, respectively. For MTHF solutions before uv irradiation, the contribution of g_{\perp} value to α^2 value is at most 3%. Although the calculation of α^2 for EtOH solid solutions is difficult because of a poor resolution of the ESR spectra, our estimation results in about 0.7. In the present calculation, we used the value of $P=0.030 \text{ cm}^{-1}$ given by Abragam, *et al.* [27] for the hyperfine structure term arising from the 3d-electrons of Cu^{2+} ions, in stead of $P=0.036 \text{ cm}^{-1}$ for that of neutral Cu atom. The values of α^2 for both solutions before uv irradiation are close to the value for pyridine-Cu(II)Y zeolite derived by Naccache *et al.* [13]. On the analogy of their discussion, the present result for MTHF solid solutions after uv irradiation indicates that the ligand molecules form a stronger σ bond with the central Cu(II) ion than that before irradiation. The present evaluation of α^2 was calculated by using the equation derived by Kivelson and Neiman [24], and may not be completely justified, since they applied the equation for the systems containing only nitrogen and oxygen ligands. However, it is true that the magnitude of ESR parameters, $g_{//}$ and $A_{//}$ reduced after uv irradiation for MTHF solid solutions, resulting in a small amount of reduction of α^2 value. This implies that the covalent σ bond is strengthened between the central metal and the ligands after uv irradiation, since $(1 - \alpha^2)$ is a measure of the strength of the bond. In the case of EtOH solution, ESR parameters are scarcely changed after uv irradiation. We infer that the ligand structure is tightly fixed in the case of polar solvents such as ethanol. Assuming that the ligand consists of two solvent molecules and two Cl⁻ ions for both MTHF and

EtOH solutions, the molecules may locate diagonally, and so the ions. In this case, the solvent molecules may coordinate a *trans* position to lower the orbital energy.

Kundu *et al.* [19] investigated the effects of annealing on the ESR parameters of $[\text{Cu}(\text{di}(\text{amH})\text{sar})](\text{NO}_3)_4$ over a wide range of temperature. The observation that the magnitude of both $g_{//}$ and $A_{//}$ reduced as raising annealing temperature led them to the conclusion that the environmental structure centered at Cu(II) undergoes a transition from dynamic to static Jahn-Teller distortions. In the present study, the magnitude of both $g_{//}$ and $A_{//}$ reduced after uv irradiation at 77 K. It is noted that the change is induced “adiabatically” by uv irradiation without raising temperature of the ligands. We infer that a sort of distortion of the environmental structure is induced by uv light in such a way that a square planer structure around Cu(II) ion before irradiation twists to form a tetrahedral structure after uv irradiation. For the solutions that stored for more than 24 hours at room temperature, subsequent uv irradiation at 77 K did not show any new ESR spectra. We infer that oxidation of the samples proceeds almost completely during storage and that CuO or tetrachloro-Cu(II) complex are produced. We confirm that Cu(II) ions observed before and after γ irradiation remain almost unchanged. In another word, electrons generated by γ irradiation don't cause any additional structural changes of the surrounding circumstances of the center metal ion. For the samples stored at room temperature longer than 1 day before uv irradiation, subsequent γ irradiation did not show the ESR spectra due to Cu^0 . This indicates that double reduction of Cu(II) by generated electrons does not occur. After worming the irradiated samples at room temperature, ESR spectra at 73 K were the same as those before uv irradiation at 77 K, indicating Cu(II)²⁺ ion revive in the ligands. This contrasts to the results that Ag⁰ atoms condensate at room temperature [8].

Finally, we refer to the solvent radicals produced after uv irradiation. In γ irradiated solid solutions, the ion-molecule reaction causes the solvent radical; e.g. in MTHF solid solution, ionization of the molecule results in the cation where positive charge localizes on oxygen atom. Then, the cation interacts with the adjacent MTHF molecule to abstract hydrogen at position 2, leaving unpaired density at position 2. Similar ion-molecule reaction occurs in irradiated EtOH solid solution, producing the alkyl radical. In the present cases, direct ionization of the solvent molecules never occur after uv irradiation in the solid solution. A possible explana-

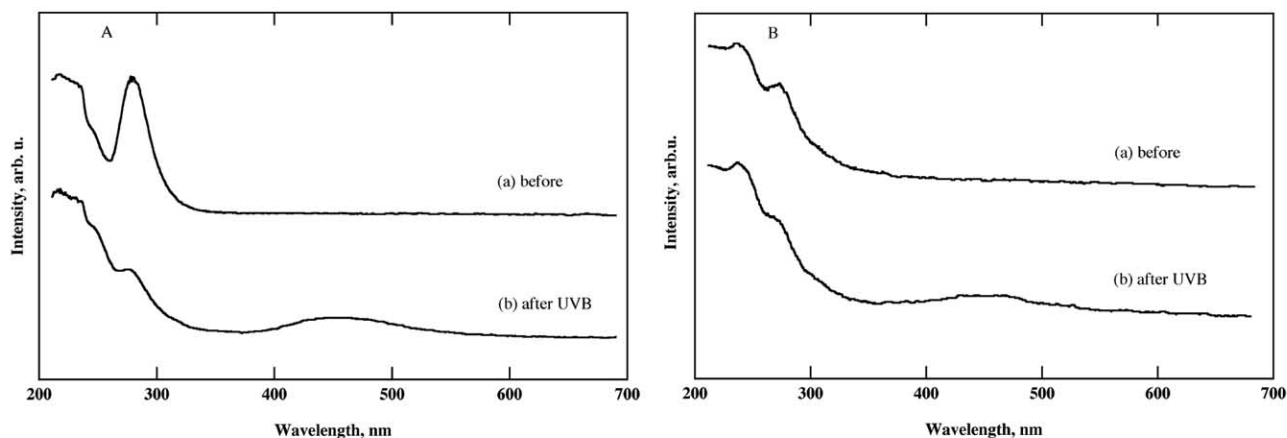


Fig. (3). Optical absorption spectra observed at 77 K before (a) and after (b) uv irradiation for the solid solutions of MTHF (A) and EtOH (B) containing 10^{-1} M CuCl with 0.2 ml HCl per solvent of 10 ml, respectively. UV irradiation was carried out at 77 K by using the UVB lamp that emits the light of maximum intensity at 310 nm with a half-height width of about 40 nm. The maximum total dose for UV irradiation was typically 1.2 J/cm^2 .

tion is that electron density is partly transferred from the ligand molecules in an excited state of Cu(II) complex, leaving cationic states of the ligand molecules that immediately take part in an ion-molecule reaction with adjacent, free MTHF molecule. However, further study should be carried out to elucidate the radical formation mechanism.

Optical Properties

In the previous section, we have reported the new set of four ESR lines on the high-field side after uv irradiation that has been ascribed to Cu(II) ions in the new ligand configuration produced *via* an exciplex state. In order to obtain further evidence for exciplex formation, we report in this section the optical properties induced by uv irradiation.

The absorption spectra observed at 77 K before and after UVB irradiation for solid solutions of MTHF and EtOH containing 10^{-1} M CuCl with 0.2 ml HCl per solvent of 10 ml are shown in Figs. (3A and B), respectively. The absorption spectra obtained after γ irradiation subsequent to uv irradiation were the same as those obtained previously [10].

It is clear in Fig. (3A) that an absorption band at 280 nm is observed in MTHF solution before uv irradiation and that after uv irradiation, this band reduces in the intensity with concomitant appearance of a new, broad band in the wavelength region of 400-500 nm. The new band is almost similar to bands C₂ and C₃ that were observed after γ irradiation in the previous study [10]. The new absorption band corresponds to the new set of four ESR lines after uv irradiation.

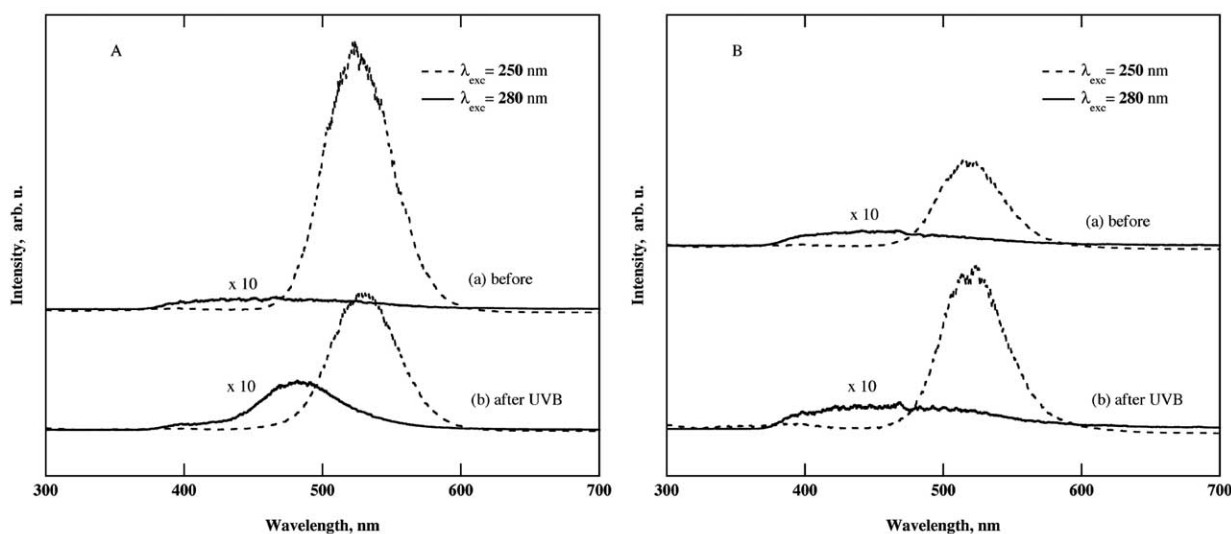


Fig. (4). Emission spectra observed at 77 K before (a) after uv irradiation (b) for the solid solutions of MTHF (A) and EtOH (B) containing 10^{-1} M CuCl with 0.2 ml HCl per solvent of 10 ml, respectively. The broken and solid lines represent the emission spectra observed by using the excitation light with $\lambda_{\text{exc}}=250$ nm and $\lambda_{\text{exc}}=280$ nm, respectively. In order to avoid the 2nd harmonics of the excitation light, cut-off filters UV 29 and L39 were used for $\lambda_{\text{exc}}=250$ and 280 nm, respectively. The relative intensity of the emission spectra observed for $\lambda_{\text{exc}}=280$ nm to those for $\lambda_{\text{exc}}=250$ nm is 1:10. The uv irradiation was carried out at 77 K by using the UVB lamp that provides the light of the maximum intensity at 310 nm with a half-height width of about 40 nm. The total dose of uv irradiation was typically 1.2 J/cm^2 .

We ascribe the new absorption band to a CT band of an exciplex including Cu(II) ion center. The same is true for EtOH, although the absorption intensities for the bands at 280 nm are weaker than those for MTHF.

The emission spectra observed at 77 K for solid solutions of MTHF and EtOH containing 10^{-1} M CuCl with 0.2 ml HCl per solvent of 10 ml are shown in Figs. (4A and B), respectively. In MTHF solutions, the intense emission band at 520 nm induced by the light of excitation at 250 nm ($\lambda_{\text{exc}}=250$ nm) before uv irradiation reduced in the intensity after uv irradiation to about 50 %. The reduction amounted to 70 % after subsequent γ irradiation. This is consistent with the previous result [10]. With $\lambda_{\text{exc}}=280$ nm, no emission was observed before uv irradiation, but a new emission band was observed after uv irradiation at 480 nm.

In EtOH solutions, the band at 520 nm was also observed before uv irradiation for $\lambda_{\text{exc}}=250$ nm and increased in the intensity after uv irradiation about two times as much as that before irradiation. This may indicate that the exciplex emitting the light of 520 nm is formed by uv irradiation in association with ligand polar solvent molecules such as EtOH. For $\lambda_{\text{exc}}=280$ nm, the result indicates that the emission was scarcely changed after uv irradiation. This result agrees with the present ESR result that any spectral change was not clearly observed in the spectral profile for EtOH solutions. The emission band profile observed in this study after the subsequent γ irradiation was consistent with the results reported previously [10].

The excitation spectra monitored at 520 nm for both MTHF and EtOH solutions after uv irradiation showed that an absorption band centered at about 270 nm with a half-height width of about 40 nm was observed.

Considering the present results of ESR and optical properties together with the previous results [10], the emissive, excited species can be classified into three types. This is shown schematically in Fig. (5):

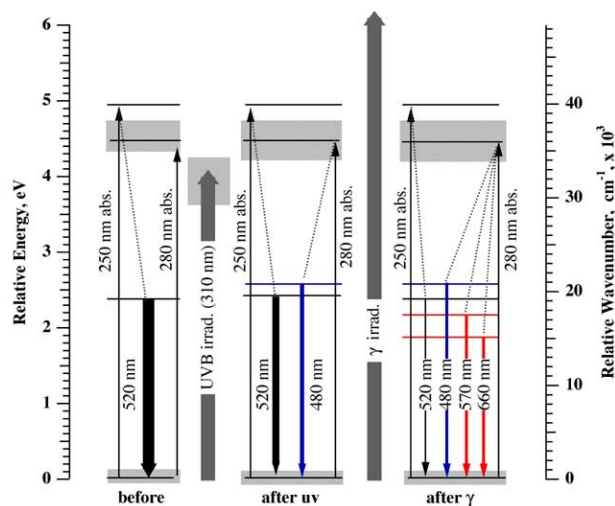


Fig. (5). Schematic diagrams of the absorption and emission energies of the species in the present study.

The first type is responsible for the absorption band at 250 nm, in which an excited metal ions associate with ligand molecules to form an ion – ligand complex that gives the

intense emission at 520 nm. The configurational structure surrounding the center Cu(I)/Cu(II) ions may be a square planer in the ground state.

The second type is produced after uv irradiation and gives rise to the absorption band at 280 nm that is responsible for the emission at 480 nm. We infer that the species of square planer structure prior to uv irradiation transforms into a tetrahedral structure after uv irradiation.

The third type is produced after γ irradiation. This gives rise to the absorption band at 280 nm and is responsible for the emission bands at 570 nm and 660 nm for MTHF, while the emission bands at 650 nm and 700 nm for EtOH. The reduction in the intensity of the emission band at 520 nm after γ irradiation is supposed to be a consequence of conversion of Cu^+ ions to Cu^0 atoms. The ESR spectrum of Cu^0 atoms produced by γ irradiation showed the duplicate quartet that was not so symmetric as the one for Au^0 , being not an axial one. This implies that the coordination of the ligand of Cu^0 close to octahedral rather than tetrahedral.

The present results of the ESR, optical absorption, emission and excitation measurements lead us to infer that ionic species including Cu(II) ion forms an exciplex between the ligand molecules during uv irradiation and that the new complex is stable at 77K. This is analogous to our previous interpretation that an exciplex forms between Cu^+ and the ligand molecules, giving rise to absorption bands C_7 and/or C_6 and the emission band at 520 nm [10].

CONCLUSIONS

The ESR properties of the species in MTHF and EtOH solid solutions observed at 73 K before and after uv irradiation in present study were attributed to an Cu(II) ion with the unpaired electron density on $3d^9$ orbital in the ligand coordinated to the ion. The spectral changes of the ion observed after uv irradiation were ascribed to a transformation of the previous species into a new species which has stronger σ bonding between the ion and the ligand.

The optical absorption and emission properties of the solutions before and after uv irradiation obtained in this study showed evidence for the formation of the new complex induced by uv irradiation. It was shown that this reaction occurred *via* an excited state of the previous species that showed an absorption band at around 280 - 310 nm corresponding to C_6 band that was referred in the previous study. We inferred that the new exciplex produced after uv irradiation must be converted internally to an emissive state, being followed by the emission at 480 nm. We tentatively proposed that the species prior to uv irradiation had a square planer structure, while after uv irradiation it was transformed into a species that was twisted into a tetrahedral direction. The solvent radicals were also observed after uv irradiation, indicating that an ion-molecule reaction occurs in such a way that the ligand solvent molecule in a cationic state by participating a stronger σ bonding with a Cu(II) ion reacts with an adjacent, free solvent molecule.

γ irradiation subsequent to uv irradiation caused no change in the spectra due to the new species, indicating that electrons generated by γ irradiation didn't react with the species. We confirmed that the structural transformation of the

species before and after uv irradiation was reversible on warming to room temperature. Finally, we also confirmed in this study that the spectrum due to Cu^0 atoms was observed after γ irradiation subsequent to uv irradiation.

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