# Ligand Effects on ESR and Optical Properties of Gold Atoms in $\gamma$ Irradiated Organic Solid Solutions at 77 K

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Ligand effects on ESR and optical properties of $Au^0$ atoms produced at 77 K in $\gamma$ irradiated solid solutions of AuCl/MTHF and AuCl/EtOH with and without HCl were investigated. Four groups of ESR lines were observed at 73 K more clearly around the magnetic fields at about 250, 280, 340, and 400 mT for both $\gamma$ irradiated MTHF and EtOH solid solutions with HCl than those without HCl. The values of $a$ and $g_J$ calculated by Breit−Rabi analysis showed a remarkable dependence on the solvent polarity. It was confirmed that the signals were the hyperfine quartet corresponding to the transitions between the Zeeman levels of $Au^0$ atoms with nuclear spin of $^3/_2$ in the ground state, $2S_{1/2}$. It was also confirmed that $Au^0$ atoms produced after $\gamma$ irradiation were located in the nuclear environment of isotropic interaction with surrounding ligand molecules. Delocalization of the unpaired spin density of $Au^0$ onto ligands is found to be as large as one in the case of $Cu^0$ atoms. Our previous hypothesis of the occurrence of configuration mixing of d valence orbital into the wave function of the atom in its $2S_{1/2}$ was strongly supported. The dependence of the ESR, optical absorption, and the steady-state emission and excitation characteristics on solvent polarity was cleared in this study. We observed two kinds of emissions i.e., a band at 385 nm and a set of emission bands at 456, 482, 484, and 520 nm. These correspond to two bands out of the six kinds of emissions observed previously. The bands were attributed to exciplex $(Au^0 \cdot Ln \cdots Au^+)^*$ and the excited $Au^0$ atoms trapped in a large cavity, respectively. The negative counterion of $Au^+$ of the gold compound plays an important role for the formation of the exciplexes.

## Introduction

It is well-known that some metal ions play important roles for the response processes in biological systems. Many kinds of metal ions and/or atoms, therefore, have long been the targets of various studies to elucidate the mechanism of controlling the their function, so that a lot of experimental results keep being reported until now. 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, i.e., $Ag^0$, $Cu^0$, and $Au^0$ that were produced radiation chemically by reducing their mono cations in solid solutions.[1−8] When a dilute solid solution of metal ions in aqueous or organic solvent is irradiated by $\gamma$ rays at a low temperature, electrons that are generated by ionization of solvent molecules reduce metal ions to form metal atoms in the original sites that the ions occupied. This method is convenient for the investigation of interactions between solutes−solutes and/or solutes−solvents in complicated systems, such as biological systems, because the metal atoms locate in the same environments in which they were produced and are distributed almost uniformly in condensed matters.

As a series of our studies on $Ag^0$ and $Cu^0$ atoms, we have already been studying $Au^0$ atoms.[6,8] The first ESR report on $Au^0$ atoms was presented by us for the two sets of (solutes/

solvents) combinations of $AuClP(C_2H_5)_3$/2-methyltetrahydrofuran (MTHF) and AuCN/10 M NaOH.[6] We have confirmed the formation of $Au^0$ atoms in the solid solutions by observing the characteristic ESR lines of $Au^0$. The values of hyperfine splitting, $a$, and g-factor of $Au^0$ atoms were calculated by using Breit−Rabi equations and the values of relative shift of those from the free atoms, i.e., $(a − a_{free})/a_{free}$ and $(g_J − g_{Jfree})$ were compared with the values obtained for the case of $Ag^0$ and $Cu^0$. It turned out from the relative shift of $a$ that the amount of delocalization of the spin density of $Au^0$ onto ligands is similar to that of $Ag^0$, but less than that of $Cu^0$. The relative shift of the g-values was positive, being similar to the case of $Cu^0$, though a negative shift was obtained for $Ag^0$. These results indicate that the admixture of the wave function of the atom in its ground state, i.e., $2S_{1/2}$ into d orbital. The optical properties of $Au^0$ atoms were originally investigated and reported by us for the case of the combination of the $AuClP(C_2H_5)_3$/MTHF by carrying out the observations of the optical absorption, steady-state emission and excitation, and the time-resolved fluorescence spectra.[8] From the optical results, three types of exciplexes $(Au^+ \cdot Ln)^*$, $(Au^0 \cdot Ln \cdots Au^+)^*$, $(Au^0 \cdot Ln)^*$, and the excited gold atom $(Au^0)^*$ were proposed. The formation mechanism of those species was also presented.

To elucidate the ligand effects on the ESR and optical properties of $Au^0$ atoms in solid solutions we have further investigated the ESR, optical absorption, and the steady-state

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emission and excitation spectra for the four sets of (solutes/solvents) combination of AuCl/MTHF and AuCl/EtOH with and without HCl. We discuss here the ligand effects in comparison with the previous results of $Au^0$ atoms in $AuClP(C_2H_5)_3$/MTHF and AuCN/10 M NaOH in solid solutions as well as $Ag^0$ and $Cu^0$ atoms.

## Experimental Section

AuCl of stated purity of more than 99.9% was purchased from Sigma Aldrich Japan and used without further purification. Reagent-grade ethanol (EtOH) and MTHF were supplied from Nacalai Tesque. MTHF was distilled fractionally before sample preparation so that no optical absorption due to its chemical additives was observed in the region of wavelengths longer than 230 nm. An amount of 5 mL of MTHF or EtOH was first bubbled by $N_2$ gas sufficiently to remove oxygen molecules in the solvents before the solutes were added. We continued bubbling and stirring the solutions and prepared two kinds of samples for each solvent: one was made without hydrochloric acid (HCl), and the other with HCl (35% in content) of about 0.09 mL for each solution. The color of the solutions changed from dark yellow to light yellow after addition of HCl. The solute was dissolved more abundantly in the solvents with HCl. The top, clear part of each colloidal solution was used for sample preparation. The solutions were transferred into ESR tubes of 4 mm in the inner diameter for ESR, emission, and excitation measurements and optical cells of 1 mm in the light path length for optical absorption measurements and then immersed into liquid nitrogen. The samples were $\gamma$ irradiated at 77 K at a dose rate of 16.0 kGy $h^{-1}$. Total dose was typically 32 kGy. After $\gamma$ irradiation, all of the samples were illuminated with light of wavelengths longer than 540 nm from a 500 W halogen lamp through an interference filter (Toshiba O-54) in order to photobleach trapped electrons. The procedures of sample preparation were almost the same as in our previous studies.[8] To remove ESR signals due to H atoms produced and trapped in a Suprasil quartz tube, the drops of solutions were directly dropped into liquid nitrogen to produce spherical glasses of about 1.5 mm in diameter.[9] For each solution, 10 or more spheres were transferred into a vial of 1 cm³ volume in liquid nitrogen and irradiated by $\gamma$ rays at 77 K. After $\gamma$ irradiation, the spherical samples were transferred into unirradiated Suprasil quartz ESR tubes in liquid nitrogen and used for measurement after photobleaching as mentioned above. ESR measurements with the use of an X-band microwave spectrometer (JEOL) were carried out at 73 K by bubbling helium gas into liquid nitrogen in an ESR Dewar to avoid bubbles from liquid nitrogen. The experimental apparatus and procedures for the optical absorption measurements at 77 K were described elsewhere.[1,2] Emission and excitation spectra were measured at 73 K with the use of a Hitachi fluorescence spectrophotometer (model F-4500). Color filters, for example UV22, UV29, UV30, UV34, UV35, L42, Y44, Y48, were used for the removal of scattered excitation light in the measurements. We also measured the phosphorescence spectra with use of the same spectrophotometer.

## Results and Discussion

**ESR Spectra.** The ESR spectra observed at 73 K for MTHF and EtOH solid solutions dissolving 0.01 M AuCl are shown in Figure 1A and B, respectively. In these figures, spectra (a) and (b) were obtained for each solution without HCl and with HCl, respectively. For the case of solutions without and with HCl, no ESR signal was observed before $\gamma$ irradiation, as shown by dotted lines in Figure 1A(a) and (b) and B(a) and (b). After
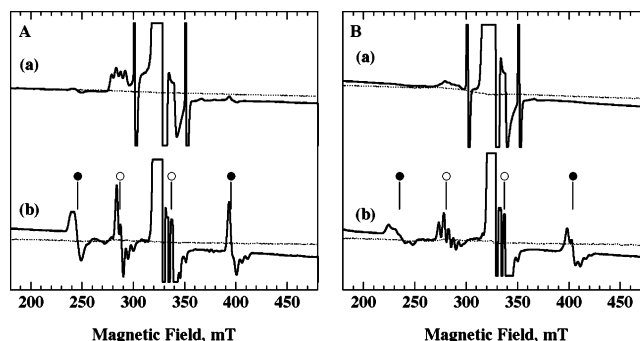


**Figure 1.** ESR spectra observed at 73 K for solid solutions of MTHF (A) and EtOH (B) containing 0.01 M AuCl without HCl (a) and with 0.09 mL HCl per solvent of 5 mL (b). $\gamma$ irradiation was carried out at 77 K, and the total dose was 32 kGy. The dotted and solid lines represent the spectra before and after $\gamma$ irradiation, respectively. For the case of the solutions with HCl (b), the sphere samples with a diameter of ca. 1.5 mm were used.[9] The values of $a$ and $g_J$ were calculated by the Breit−Rabi equation using the set of the ESR lines represented as (●). The remaining set of the magnetic fields of the hyperfine quartet corresponding to an atom with nuclear spin of $^3/_2$ in the ground state, $2S_{1/2}$, was obtained by using the calculated values of $a$ and $g_J$ and are represented as (○) in the spectra.

$\gamma$ irradiation, two weak ESR lines at 245 mT and 395 mT were observed for MTHF solution without HCl but were not observed for EtOH solution without HCl as shown by solid lines in Figure 1A(a) and B(a), respectively. As being discussed later, the ESR lines are attributed to $Au^0$ produced radiation chemically in the solid solutions. Two strong, sharp ESR absorption lines observed at 283 mT and 352 mT for both cases are due to H atoms that were produced and trapped in a Suprasil quartz tube. These signals can be removed by employing the method of spherical samples.[9] The ESR lines observed for MTHF and EtOH solutions with HCl are shown in Figure 1A(b) and B(b), respectively.

Four groups of ESR absorption signals were observed more clearly around the magnetic fields of 250, 280, 340, and 400 mT for both MTHF and EtOH solid solutions with HCl than those without HCl. A superhyperfine structure is distinguished in these ESR lines. It is noted that the superhyperfine structure for EtOH solution is especially more remarkable in comparison with MTHF solution. It is difficult to conclude at this stage from where the superhyperfine structure originated. However, if this originates from the $Cl^-$ ion of nuclear spin of $^3/_2$ around $Au^0$ atoms, more than one $Cl^-$ ion may be associated. We tentatively infer that two nuclei of $Cl_2^{•-}$ radical anions produced in the vicinity of $Au^0$ atoms are responsible for the superhyperfine structure. The fact that the color of the solutions changed after addition of HCl implies formation of complexes between $Au^+$ ions and excess $Cl^-$ ions. We ascribe the spectra, consisting of four groups of ESR lines at, e.g., 250, 280, 340, and 400 mT, to $Au^0$ atoms produced radiation chemically in the solutions according to the following argument.

Natural gold has only one stable isotope, $Au^{197}$, which has a nuclear spin of $^3/_2$, and, in free state, has a magnetic moment of 2.00412 nuclear magnetons. Thus, the ESR of $Au^0$ exhibits hyperfine quartet spectrum. The energy levels of the hyperfine structure of the ground state, $2S_{1/2}$, are described by the following Breit−Rabi equation in a similar fashion to $Cu^0$ atoms with a nuclear spin of $^3/_2$:[7,10,11,12]

$$W\left(\pm\frac{1}{2}, m\right) = -\frac{\Delta W}{8} + g_I\beta H_I m \pm \frac{\Delta W}{2}(1 + mx_i + x_i^2)^{1/2} \quad (1)$$

where $\Delta W$ is the energy of the hyperfine splitting in zero

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**TABLE 1: Comparison of the Values of $a$ and $g_J$ of $Au^0$ Atoms for Our Present Studies with Those for the Previous Studies[a]**

| matrix | solute | $a$ (MHz) | $\delta(a)/a_{\text{free}}$[b] (%) | $g_J$ |
|---|---|---|---|---|
| MTHF + HCl[c] | AuCl | 2828.5 ± 4.0 | −53.7 | 2.017 ± 0.002 |
| $C_2H_5OH$ + HCl[c] | AuCl | 3167.5 ± 5.5 | −48.1 | 2.015 ± 0.002 |
| MTHF[d] | $AuClP(C_2H_5)_3$ | 5025.3 ± 6.5 | −17.7 | 2.107 ± 0.001 |
| 10 M-NaOH[d] | $AuClP(C_2H_5)_3$ | 5144.7 ± 4.0 | −15.8 | 2.257 ± 0.002 |
| $C_{11}H_{24}$[e] | | 5909.0 ± 5.7 | −3.24 | 2.00422 ± 0.00060 |
| $H_2O$[e] | | 6105.6 ± 3.2 | −0.02 | 2.00306 ± 0.00015 |
| $C_2H_5OH$[e] | | 4146.7 ± 13.1 | −32.1 | 2.07150 ± 0.00100 |
| free[e] | | 6107.1 ± 1.0 | | 2.00412 ± 0.00012 |

[a] The set of transitions $(F = 1, m = 1) \leftrightarrow (F = 2, m = 2)$ and $(F = 2, m = -2) \leftrightarrow (F = 2, m = -1)$ was used for the calculation of $a$ and $g_J$ values by using the Breit−Rabi equation in our present studies  [b] $\delta(a) = a - a_{\text{free}}$, where $a_{\text{free}} (= \Delta\nu_{\text{free}})$ is the hyperfine structure splitting of a free Au atom[11,12] in zero magnetic field: $a_{\text{free}}(^{197}\text{Au}) = 6107.1$ MHz. [c] Present work. [d] Our previous work.[6] [e] Zhitnikov's work.[11]

magnetic field; $x_i = (g_J - g_I)\beta H_i/\Delta W$, $g_I$ and $g_J$ are the gyromagnetic ratio for the nucleus ($g_I = -0.51 \times 10^{-4}$ for $Au^0$) and for the electron shell, respectively; $\beta$ is the Bohr magneton; $H_i$ is the resonant magnetic field; $m$ is the magnetic quantum number of the total moment of the atom $\boldsymbol{F} = \boldsymbol{J} + \boldsymbol{I}$, where $\boldsymbol{J}$ and $\boldsymbol{I}$ are the moments of the electrons and of the nucleus, respectively. According to the Zeeman levels of the hyperfine structure of $Au^0$ with nuclear spin of $^3/_2$, four groups in ascending order of magnetic field ($H_1$, $H_2$, $H_3$, $H_4$) correspond to transitions, $(F = 1, m = 1) \rightarrow (2, 2)$, $(1, 0) \rightarrow (2, 1)$, $(1, -1) \rightarrow (2, 0)$ and $(2, -2) \rightarrow (2, -1)$, respectively. One obtains from eq 1 the following relations for those transitions:

$$h\nu = ha\left\{\frac{1}{2}(1 + x_1 + x_1^2)^{1/2} + \frac{1}{2}(1 + x_1) + \frac{g_I\beta H_1}{ha}\right\} \quad (2)$$

$$h\nu = ha\left\{\frac{1}{2}(1 + x_2 + x_2^2)^{1/2} + \frac{1}{2}(1 + x_2)^{1/2} + \frac{g_I\beta H_2}{ha}\right\} \quad (3)$$

$$h\nu = ha\left\{\frac{1}{2}(1 - x_3 + x_3^2)^{1/2} + \frac{1}{2}(1 + x_3)^{1/2} + \frac{g_I\beta H_3}{ha}\right\} \quad (4)$$

$$h\nu = ha\left\{\frac{1}{2}(1 - x_4 + x_4^2)^{1/2} - \frac{1}{2}(1 - x_4) + \frac{g_I\beta H_4}{ha}\right\} \quad (5)$$

where $a$, defined as $\Delta W = ah$ in our representation, is the value of the hyperfine splitting; $h$ is the Planck's constant. The values of the four resonance magnetic fields ($H_i$, $i = 1, 2, 3, 4$) at constant microwave frequency, $\nu$, are obtained by the ESR measurement. The values of $a$ and $g_J$ can be obtained from different pairs of lines in the same spectrum. Because the two groups of the ESR lines at $H_2$ and $H_3$ have some complex superhyperfine structures, we used $H_1$ and $H_4$ for MTHF and EtOH solid solutions with HCl in order to calculate the values of $a$ and $g_J$, which are represented by (●) in Figure 1A(b) and B(b), respectively. With the use of the calculated values of $a$ and $g_J$, we could calculate an inner set of the magnetic fields, $H_2$ and $H_3$. These are represented by (○) in the ESR lines. It is clear that the observed ESR lines are located at the same position as the calculated magnetic fields for both MTHF and EtOH solid solutions with HCl. This indicates that the four groups of the ESR lines are due to the hyperfine quartet corresponding to the transitions between the Zeeman levels of the atom with a nuclear spin of $^3/_2$ in the ground state, $^2S_{1/2}$ of $Au^0$ atoms, and that the atoms located in the nuclear environment of isotropic interaction with surrounding ligand molecules. In this circumstance, the Zeeman splitting energy levels of the hyperfine structure are adequately expressed by the Breit−Rabi eq 1, and the magnetic interaction between nuclear spin $\boldsymbol{I}$ and electronic angular momentum $\boldsymbol{J}$ is represented as intermediate coupling.[12]

The calculated values of $a$ and $g_J$ by using eqs 2 and 5 at $H_1$ and $H_4$, respectively, for MTHF and EtOH solutions are listed

in Table 1. The results of the previous study[6] and Zhitnikov's ones[11] are also listed together for the comparison. It is noted that the values of $a$ obtained in the present study for the systems of AuCl/MTHF + HCl and AuCl/EtOH + HCl are smaller than those obtained in the previous study for the systems of AuClP-$(C_2H_5)_3$/MTHF and AuCN/10 M NaOH. This suggests that the interaction between $Au^0$ atoms and the neighboring local field is stronger in the present system than in the previous system. The relative shifts of the values of $a$, i.e., $\delta(a)/a_{\text{free}}$ where $\delta(a) = a - a_{\text{free}}$ are −53.7% and −48.1% for the MTHF + HCl and EtOH + HCl solutions in this study, respectively. The large negative shifts of $a$ in the present system, which is as large as that in the case of $Cu^0$[7], indicate that the electronic delocalization onto ligand molecules amounts are more than in the previous system of solutions.

It is the characteristic ligand effect in the present system that the negative shift rate, $\delta(a)/a_{\text{free}}$, depends on the polarity of the solutions a little more than in the case of the $Cu^0$ system.[7] The other ligand effect in the present study is that the value of $a$ obtained for MTHF + HCl solutions is smaller than that obtained for EtOH + HCl solutions and that the value $g_J$ obtained for MTHF + HCl solutions is much larger than that obtained for EtOH + HCl solutions. This indicates that the spin density inclines to increase more on $Au^0$ atoms in the polar solutions than in the nonpolar solutions. This is one of the characteristic ligand effects observed in this study because the correlation between the values of $a$ and $g_J$ and solvent polarity was obscure in the previous study. As shown in Table 1, the sign of values $g_J - g_{\text{free}}$, is positive in the present study. The same is true for the previous study[6] and also for $Au^0$ atoms condensed in $C_2H_5OH$ matrix.[11] This result supports the hypothesis of occurrence of configuration mixing of the d valence orbital into the wave function of the atom in its $^2S_{1/2}$.

**Optical Absorption Spectra.** The optical absorption spectra before $\gamma$ irradiation were subtracted from those after irradiation. The difference spectra thus obtained at 77 K for MTHF and EtOH solid solutions containing AuCl of 0.01 M are shown in Figure 2A and B, respectively. In these figures, spectra (a) and (b) were obtained for each solution without HCl and with HCl, respectively. The spectra obtained before and after $\gamma$ irradiation are also shown by broken and dotted lines, respectively.

The optical absorption spectra for AuCl/MTHF solutions without and with HCl obtained and shown in Figure 2A(a) and (b) in this study are almost similar to the previous spectra for $AuClP(C_2H_5)_3$/MTHF solutions[8] except for two points: first, an absorption band at 320−330 nm was observed clearly for the present cases before $\gamma$ irradiation, which was hardly observed for the previous ones, and second, the absorption bands were observed at 340−380 nm in the difference spectra, which were not for $AuClP(C_2H_5)_3$/MTHF solutions.[8] According to the fact that the absorption band of the $Cl_2$ in gas phase lies at 330 nm,

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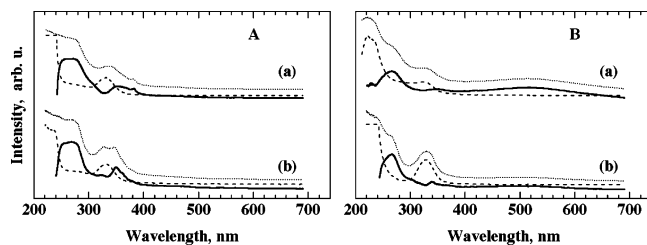*J. Phys. Chem. B, Vol. 109, No. 40, 2005* **18945**



**Figure 2.** Absorption spectra observed at 77 K for solid solutions of MTHF (A) and EtOH (B) containing 0.01 M AuCl without HCl (a) and with HCl of 0.09 mL per solvent of 5 mL (b). $\gamma$ irradiation was carried out at 77 K and the total dose was 32 kGy. The broken and dotted lines represent the spectra before and after $\gamma$ irradiation, respectively. The solid lines represent the difference spectra.

the absorption band at 320−330 nm seems to originate from a molecular complex of Cl⁻ ions formed in the solutions before $\gamma$ irradiation. After $\gamma$ irradiation, a broad, intense absorption spectrum that consists of two or more bands was observed in the UV region of 260−280 nm for MTHF solutions without and with HCl. This is similar to the case for AuClP(C₂H₅)₃/ MTHF solutions.[8] In addition to these bands, a broad absorption band was observed after $\gamma$ irradiation at 320−400 nm with a peak at 340 nm and a long tail extending to 400 nm for AuCl/ MTHF solution without HCl as shown by the dotted line in Figure 2A(a). In the previous case for AuClP(C₂H₅)₃/MTHF solutions,[8] the broad absorption band appeared in the NUV region of 320−380 nm in the case of higher Au⁺ concentration. A weak absorption peak was also observed at 390 nm in the present case. For the solution with HCl after $\gamma$ irradiation, the absorption band with two peaks at 320 and 350 nm, together with another very weak peak at around 380 nm, were observed as shown by the dotted line in Figure 2A(b). The intensity of the absorption band at 340−350 nm increases much more for the solution with HCl than without HCl. This implies that Cl⁻ ions are associated with the absorption band. Because Ogura et al.[13] reported that Cl₂•⁻ radical anions produced in pulse-irradiated aqueous solutions of NaCl at high concentration show an absorption band at 340 nm, we infer that the absorption band with a peak at 340 nm observed in the present study is ascribed to Cl₂•⁻ radical anions[13] produced in $\gamma$ irradiated solid solutions.

The absorption spectra for AuCl/EtOH without and with HCl were investigated for the first time in the present study. The absorption bands were observed in the region of wavelength shorter than 240 nm for both EtOH solutions without and with HCl before $\gamma$ irradiation. After $\gamma$ irradiation, another absorption band appeared at about 270 nm. It is noted that the absorption bands in the UV region show some solvent dependence. The absorption band at 330 nm was also observed for the EtOH solutions before and after $\gamma$ irradiation. This is similar to the case of MTHF solutions. The intensity of the absorption band at 330 nm decreases a little after $\gamma$ irradiation for the solution with HCl but not for the solution without HCl. This supports the hypothesis of formation of a complex of Cl⁻ ions in the solutions before $\gamma$ irradiation. In the present study, no other absorption band appeared newly after irradiation in the NUV region in EtOH solutions except the weak one at 340 nm. For the EtOH solid solutions without HCl, a broad, very weak absorption band appeared after irradiation at around 520 nm, although it was not observed for the solutions with HCl.

On the basis of the ESR evidence of the formation of Au⁰ in the MTHF and EtOH solid solutions with HCl, we attribute the absorption bands observed in the UV and NUV regions in the difference spectra to Au⁰ atoms and/or the complexes formed between Au⁰ atoms and ligand molecules in the $\gamma$ irradiated
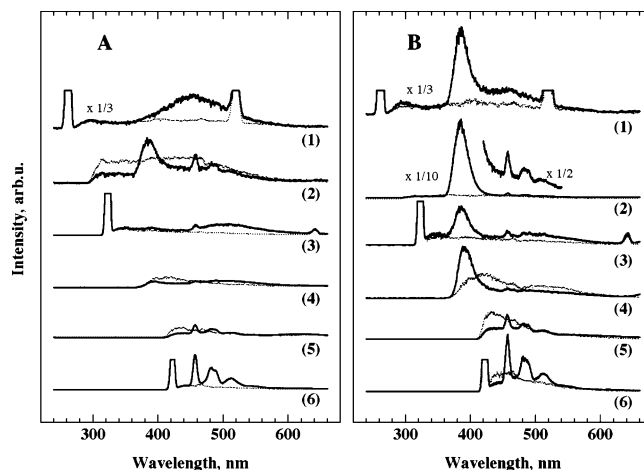


**Figure 3.** Steady-state emission spectra observed at 73 K for solid solutions of MTHF containing 0.01 M AuCl without HCl (A) and with HCl of 0.09 mL per solvent of 5 mL (B). $\gamma$ irradiation was carried out at 77 K, and the total dose was 32 kGy. The dotted and solid lines represent the spectra before and after $\gamma$ irradiation, respectively. The wavelengths of light used for excitation are (1) 260, (2) 280, (3) 320, (4) 350, (5) 390, and (6) 420 nm. The ordinates represent emission intensity in arbitrary unit.
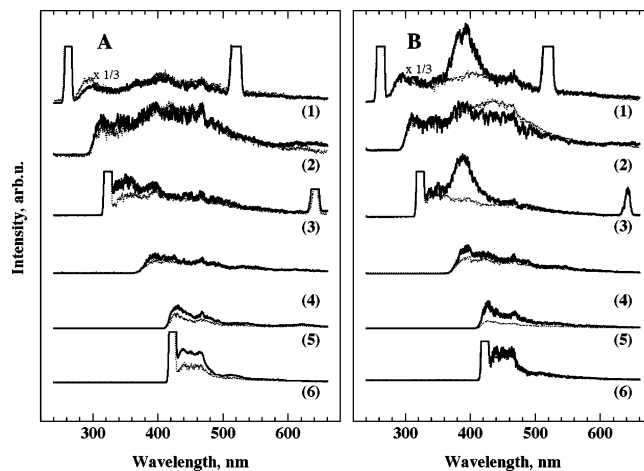


**Figure 4.** Steady-state emission spectra observed at 73 K for solid solutions of EtOH containing 0.01 M AuCl without HCl (A) and with HCl of 0.09 mL per solvent of 5 mL (B). $\gamma$ irradiation was carried out at 77 K, and the total dose was 32 kGy. The dotted and solid lines are the spectra for the samples before and after $\gamma$ irradiation, respectively. The wavelengths of light used for excitation are (1) 260, (2) 280, (3) 320, (4) 350, (5) 390, and (6) 420 nm. The ordinates represent emission intensity in arbitrary units.

solid solutions at 77 K. The complexes may consist of Au⁰ atoms in the excited states and neighboring ligand species involving two or more chloride atoms. These absorption bands were red-shifted and broadened in comparison with those in rare gas matrixes, indicating a strong ligand−Au⁰ interaction that was similar to the previous case for AuClP(C₂H₅)₃/MTHF solutions.

**Steady-State Emission and Excitation Spectra.** The steady-state emission spectra were obtained at 73 K for the irradiated MTHF and EtOH solid solutions containing 0.01 M AuCl without and with HCl and are shown in Figure 3A and B, and Figure 4A and B, respectively. The wavelengths of excitation light ($\lambda_{exc}$) were chosen from the wavelength region of the prominent absorption bands. In these figures, the peaks observed at 260 and 520 nm in spectrum (1) and at 320 and 640 nm in spectrum (3) are due to the excitation light passed through the cutoff filters (UV29, UV34) and its 2nd subharmonic oscillation,

respectively. The peaks observed at 420 nm in spectrum (6) are also due to the excitation light passing through the cutoff filter (Y44).

In the case of the $\gamma$ irradiated AuCl/MTHF without HCl and with HCl, we observed two kinds of emissions, i.e., a band at 385 nm and a set of emission bands at 456, 482, 484, and 520 nm that correspond to two bands out of the six kinds of emissions observed previously for the case of AuClP(C$_2$H$_5$)$_3$/MTHF solution.[8] The former emission band at 385 nm was observed for $\lambda_{exc} = 280$ nm for the solutions without HCl and was observed for $\lambda_{exc} = 260, 280, 320$, and 350 nm for the solutions with HCl. The maximum intensity of this emission was obtained for $\lambda_{exc} = 280$ nm, similar to the previous observation for AuClP(C$_2$H$_5$)$_3$/MTHF solutions.[8] The latter set of emission bands with peaks at 456, 482, 484, and 520 nm has the characteristic spectral structure that corresponds to a mirror image of the absorption spectrum of Au$^0$ atoms in the gas phase. We have already ascribed the band to the emissions from the excited Au$^0$ atoms (Au$^0$)* that are trapped in a large cavity in which Au$^0$ atoms in their excited state interact very weakly with the surrounding solvent molecules. This set of emission bands was always observed in the present case for $\lambda_{exc} = 280, 320, 350$, and 420 nm. The maximum intensity of the emissions was obtained for $\lambda_{exc} = 420$ nm. The intensity of the two kinds of emissions mentioned above was stronger for MTHF solutions with HCl than for those without HCl. On the other hand, the corresponding emissions were weaker in the intensities for the case of AuCl/EtOH solutions without and with HCl than for the case of AuCl/MTHF solutions as shown in Figure 4A and B. The relative intensity ratio of the emissions for the case of AuCl/EtOH with HCl to those for the case of AuCl/MTHF with HCl was about $^1/_3$ by estimating from the comparison of the intensity of the peaks due to the 2nd subharmonic oscillation of the excitation light at 640 nm in spectrum (3) for $\lambda_{exc} = 320$ nm in Figure 3B and 4B. The emission band at 385 nm was observed for the case of the EtOH solutions with HCl for $\lambda_{exc} = 260$ and 320 nm, but not for those without HCl. Being very weak in the intensities, the peaks of emission bands due to (Au$^0$)* were observed around at 460−480 nm for almost all excitation wavelength as shown in Figure 4. No other characteristic emission band was observed for the case of the EtOH solutions.

There are mainly three different observations between the emission spectra for the previous case of AuClP(C$_2$H$_5$)$_3$/MTHF solutions and those for the present case of AuCl/MTHF solutions without HCl and with HCl. First, the intense, broad emission band with a peak at 430 nm, corresponding to phosphorescence for $\lambda_{exc} = 280$ nm before $\gamma$ irradiation for the previous case, was hardly observed for the present cases of the solutions without and with HCl for $\lambda_{exc} = 280$ nm, except that weak phosphorescence signals were observed only for the case of the AuCl/MTHF solutions with HCl before $\gamma$ irradiation. The broad emission band extending from 400 to 500 nm with a peak around at 450 nm was observed for the MTHF solution without HCl after $\gamma$ irradiation for $\lambda_{exc} = 260$ nm, as shown by the solid line in Figure 3A(1). However, this was not phosphorescence. For the case of the AuCl/EtOH solutions with HCl before $\gamma$ irradiation, we confirmed the existence of the phosphorescence with a peak at 430 nm a little more clearly than for the case of the MTHF solutions, although it was too weak to measure the lifetime of the emission. The broad emission band with a peak at 430 nm observed before $\gamma$ irradiation for $\lambda_{exc} = 280$ nm, as shown by the dotted line in Figure 4B (2), corresponds to the phosphorescence. Thus, we confirmed in the present study that



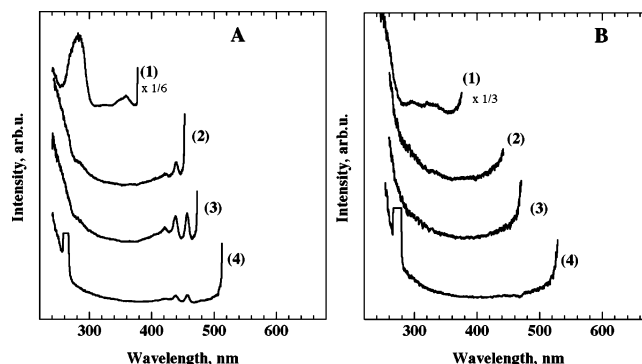**Figure 5.** Steady-state excitation spectra at 73 K of Au$^0$ produced in $\gamma$ irradiated MTHF (A) and EtOH (B) solutions containing 0.01 M AuCl with HCl of 0.09 mL per solvent of 5 mL. The excitation spectra are recorded for the peak wavelengths of emission bands at (1) 385, (2) 460, (3) 480, and (4) 520 nm. The ordinates represent emission intensity in arbitrary units.

the phosphorescence is caused by excitation of the optical absorption band at 280 nm.

Second, in the previous case of AuClP(C$_2$H$_5$)$_3$/MTHF solutions,[8] the emission spectrum consisting of three bands at 480, 520, and 580 nm was observed for $\lambda_{exc} = 320, 350$, and 390 nm and was attributed to the exciplex such as (Au$^0 \cdot Ln$)*. In the present cases of MTHF and EtOH solutions, however, the emissions were not observed.

Third, the existence of the set of emission bands with peaks at 456, 482, 484, and 520 nm could be distinguished clearly in the emission spectra immediately after $\gamma$ irradiation in the present study. Note that, in the previous study, this characteristic spectral structure could be observed only after storing the irradiated samples of the AuClP(C$_2$H$_5$)$_3$/MTHF for about 3 months in the dark at liquid nitrogen temperature. From the viewpoint of our previous conclusion that these emissions are due to (Au$^0$)* trapped in a large cavity in which they interact very weakly with the surrounding solvent molecules, (Au$^0$)* is formed more abundantly in the case of the AuCl/MTHF solutions than in AuClP(C$_2$H$_5$)$_3$/MTHF solutions. Together with the fact that the intensity of the emissions in question was stronger for the present case of the solutions with HCl than the solutions without HCl, we infer that Cl$^-$ ions are deeply associated with the formation of the (Au$^0$)*. The set of emission bands in question was not observed for $\lambda_{exc} = 260$ nm for both cases of AuCl/MTHF solutions without and with HCl. This implies that the photoionization of Au$^0$ atoms occurs around 260 nm for the case of MTHF solutions. On the other hand, the small peaks that must be the members of the group of the emissions from (Au$^0$)* were observed in spectrum (1) for $\lambda_{exc} = 260$ nm around 460 nm for the case of EtOH solutions without and with HCl, as shown in Figure 4A and B, respectively. Therefore the wavelength of the absorption band ascribed to photoionization of Au$^0$ atoms in the case of the EtOH solutions must be shorter than 260 nm, being probably at about 240 nm.

The respective excitation spectra corresponding to the emission bands observed for the $\gamma$ irradiated solutions of AuCl/MTHF with HCl and AuCl/EtOH with HCl are shown in Figure 5A and B, respectively. The excitation spectrum obtained for the monitoring wavelength ($\lambda_{mon}$) of 385 nm for AuCl/MTHF solution with HCl is almost similar to that obtained previously for the case of AuClP(C$_2$H$_5$)$_3$/MTHF solution, though the spectral structure and its relative intensity in the region of 320−380 nm is a little different. This is due to the difference in the spectral structure of the optical absorption in this region

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(see Figure 2A(b)). For the present case of AuCl/MTHF solution with HCl, the emission band at 385 nm originates mainly from the excitation around at 270–280 nm and a little from the excitation at 340 and 360 nm. On the other hand, it is confirmed that, in Figure 5B(1), the emission band at 385 nm for the present case of AuCl/EtOH solution with HCl originates mainly from the excitation at the wavelengths shorter than 270 nm and a little from the excitation around 290–300 and 320–340 nm. These correspond to the optical absorption spectra in the UV region for each solution. We should pay attention to the fact that the solvent polarity dependence of Stokes shift is shown in the spectra. The excitation spectra (2), (3), and (4) shown in Figure 5A and B were recorded at 460, 480, and 520 nm, respectively, which were close to the peaks of the characteristic emission bands in question, i.e., 456, 482, 484, and 520 nm. We have already concluded that they originate from $(Au^0)^*$ that are trapped in a large cavity where $Au^0$ atoms scarcely interact with the surroundings. The latter two wavelengths of monitoring this characteristic emission group, $\lambda_{mon} = 480$ and 520 nm, are the same as those of the wavelengths of the peaks of the other type of the emission bands at $\lambda_{max} = 480$ and 520 nm by chance. These bands were observed previously for $AuClP(C_2H_5)_3$/MTHF solutions, but not for the present case of the AuCl/MTHF solutions without and with HCl. This can be explained by the fact that the absorption bands in the NUV region at 320 and 340 nm were not observed in the excitation spectra for $\lambda_{mon} = 480$ and 520 nm, as shown in Figure 5A(3) and (4), respectively. The absorption peaks at 420, 440, and 460 nm were also observed for the present solutions for $\lambda_{mon} = 460$, 480, and 520 nm as well as in the previous case.

The fact that these absorption peaks were not observed in the present case of the irradiated EtOH solutions without and with HCl is probably because of weak emissions due to a low amount of $(Au^0)^*$ for the case of EtOH solutions. We inferred in the previous study that the absorption bands at 420, 440, and 460 nm were attributed to the transition of $Au^0$ atoms involving a forbidden transition of 5d–6s, which might be caused by configuration mixing such as spin–orbit coupling. It is certain that the present ESR study strongly supports this interpretation.

For the chemical equilibrium of $AuCl \rightleftarrows Au^+ + Cl^-$ in solutions, $Au^+$ ions locate nearer to the solvent molecules and more randomly in nonpolar solvents than in polar solvents. In the case of MTHF molecules as the solvent, they will turn the side of the oxygen atoms of MTHF toward $Au^+$ ions. However, a repulsive force between the oxygen atoms and $Cl^-$ ions may tend to keep $Au^+$ ions away from MTHF molecules. Addition of HCl in the solutions will promote this tendency, and then $Au^+$ ions are more and more isolated. Under this condition, $Au^0$ atoms produced via the electron capture of $Au^+$ ions are also isolated. This is what we call $Au^0$ atoms trapped in a large cavity. Thus, the emissions from the isolated $(Au^0)^*$ states will increase. According to the fact that the weak phosphorescence around 430 nm was observed for both the solutions of MTHF and EtOH with HCl before $\gamma$ irradiation and that the intense emission band at 385 nm was observed for those solutions after $\gamma$ irradiation, it is concluded that the emissive exciplex such as $(Au^0 \cdot Ln \cdots Au^+)^*$ is produced. Some $Cl^-$ ions must be associated with $Ln$ because of the superhyperfine structure observed in the ESR structure that suggests the possibility of two or more $Cl^-$ ions in the vicinity of $Au^0$ atoms. Because $Cl^-$ ions locate in the close vicinity of $Au^+$ ions, the emissive exciplexes such as $(Au^0 \cdot Ln \cdots Au^+)^*$ may be formed by photoexcitation much more than those such as $(Au^0 \cdot Ln)^*$. This explains the reason

the emission bands at 480, 520, and 580 nm from exciplex $(Au^0 \cdot Ln)^*$ were not observed for the present solid solutions.

Exciplex $(Au^0 \cdot Ln \cdots Au^+)^*$ formed for $\lambda_{exc} = 280$, 320, and 350 nm in the present case of the solutions mainly emits the fluorescence with peak wavelength at 385 nm rather than the phosphorescence. In the polar solvent EtOH, the $Cl^-$ ions donate an electron to the solvent molecules and $Au^+$ ions to some extent. This may be the reason that some of the peaks of the emission group from the $(Au^0)^*$ were observed around 460–480 nm for the case of EtOH solutions without and with HCl even before $\gamma$ irradiation, although the intensities were very weak. The electron donation may weaken the polarity of the solvent molecules a little. Addition of $Cl^-$ from HCl may enhance this tendency so that $Au^0$ atoms formed in the solutions with HCl interact more strongly with the surrounding solvent molecules than those without HCl. This may be the reason the photoionization of the $Au^0$ atoms has not occurred yet at 280 nm, and the emission band at 385 nm was observed even at 260 nm for the present case of the AuCl/EtOH solutions with HCl. The weak emissions for the case of the EtOH solutions compared to the case of MTHF solutions indicate that the nonradiative transitions from the excited states to the ground states occur to stabilize the exciplex for the case of the EtOH.

## Conclusion

Ligand effects on ESR and optical properties of $Au^0$ atoms produced in $\gamma$ irradiated AuCl/MTHF and AuCl/EtOH solutions with and without HCl were investigated. The four groups of ESR lines were observed around 250, 280, 340, and 400 mT for both MTHF and EtOH solutions with HCl were ascribed to the hyperfine quartet of the $Au^0$ atoms with nuclear spin of $^3/_2$ in the ground state, $2S_{1/2}$. $Au^0$ atoms produced after $\gamma$ irradiation locate in the nuclear environment of isotropic interaction with surrounding ligand nuclei. The superhyperfine structures observed in the ESR lines may be due to the spin–spin interaction between $Au^0$ atoms and the two or more $Cl^-$ ions that locate close to $Au^0$ atoms. The values of $a$ and $g_J$ calculated by Breit–Rabi analysis showed the well-known dependence on the solvent polarity that the bigger values of $a$ and the smaller values of $g_J$ are characteristic of the cases of polar solvents such as EtOH than for the cases of less polar solvents such as MTHF. The large negative shifts of $a$, i.e., $\delta(a)/a_{free}$, are $-53.7\%$ and $-48.1\%$ for the AuCl/MTHF with HCl and AuCl/EtOH with HCl solutions, respectively, which are almost similar to the case of $Cu^0$ atoms,[7] indicate that the electronic delocalization onto ligand molecules amounts to much more than in the previous system of $AuClP(C_2H_5)_3$/MTHF solutions. The positive $g_J - g_{free}$ were obtained and support the hypothesis of occurrence of configuration mixing of the d valence orbital into the wave function of the $Au^0$ atoms in $2S_{1/2}$.

The absorption bands around 270–280 nm observed after irradiation are ascribed to $Au^0$ atoms in the solutions. These bands were red-shifted and broadened compared to those in the rare gas matrixes, indicating a strong solvent–$Au^0$ interaction. The absorption band around 330–340 nm is ascribed to the exciplex that consists of $Au^0$ atoms and neighboring two or more $Cl^-$ ions and/or solvent molecules, and especially the peak at 340 nm, is tentatively ascribed to $Cl_2^{\bullet-}$ radical anions.

The emission bands observed at 385 nm is attributed to an exciplex such as $(Au^0 \cdot Ln \cdots Au^+)^*$. The emission bands observed at 456, 482, 484, and 520 nm are mainly attributed to the excited $Au^0$ atom, $(Au^0)^*$ trapped in a large cavity. In the present case of AuCl/MTHF solutions with HCl especially, the isolation of $Au^0$ atoms by $Cl^-$ ions is more remarkable than for the previous

$AuClP(C_2H_5)_3$/MTHF solutions, resulting in the increased emission from the $(Au^0)^*$. In the case of AuCl/EtOH solutions, $Cl^-$ ions behave as electron donors for the solvent molecules and $Au^+$ ions to some extent. This may cause a weak emission even before irradiation. Almost the same exciplexes may be formed in irradiated EtOH and MTHF solutions, but the intensity of the former is weaker than that of the latter. This implies that a stabilization route due to nonradiative transition exists in the case of EtOH solutions. The absorption band due to the photoionization of $Au^0$ atoms must be in the region of the wavelengths shorter than 260 nm in the present solutions.

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