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ESR of Hot Ions: Ni(I) Complex Ions Produced in Rigid Solutions by UV-Exposure

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It has been shown that univalent nickel complex ions are produced in rigid solutions by electrons released on photo-ionization of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine. These complexes have the same *g*-values as those obtained by γ-irradiation, suggesting that the univalent nickel complex ions produced on γ-irradiation can be formed as a result of the capture of near-thermal electrons by bivalent nickel complexes. Upon UV-exposure at various sample temperatures between -196 °C and -70 °C, a new chemical species with $g_{//}$ of 2.37 and $g_{\perp}$ of 2.128 has been observed, which appears to be an exchange-coupled dimer of the univalent hexaaqua nickel complex ions.

Paramagnetic ions which are produced in diamagnetic inorganic metal complexes upon γ-ray irradiation, are referred to as the hot ions.[1,2] Investigations have been carried out in this laboratory on metal ions such as Co, Ni, Pd, Pt, Rh, Ir, Cu, Zn, Cd, Hg, and Tl, in order to clarify the distortion of the lattice structure of the host compounds, which is caused by the formation of reduced or oxidized metal complex ions.

This paper deals with the hot ion of nickel which will be compared with the case of Pd and Co. From the viewpoint of the distortion of the ligand field, Pd(II), which takes a square planar structure, presents an extreme case where the hot ion is stabilized without appreciable change of the symmetry of ligand field in the process of one electron reduction. In the case of Ni(II), however, the original octahedral structure becomes distorted to the tetragonal one by the formation of Ni(I), which may be caused by the Jahn-Teller effect. The technique of investigation adopted in this experiment is almost the same as that in the case of Pd(II), *i.e.* the reaction of Ni(II) complex ions with the photoelectrons from *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in rigid solutions. We have also examined the effect temperature of the rigid solutions on the formation of Ni(I) complex ions during and after UV-exposure.

Experimental

Nickel(II) chloride hexahydrate, purified by the anion exchange method, was dissolved into a glassy solvent, a mixture of ethylene glycol and water (2: 1 v/v). Ethylenediamine (en), 2,2'-bipyridyl (bpy), or 1,10-phenanthroline (phen) was added to the nickel(II) solution as a ligand. The molar ratio of nickel(II) chloride to each ligand was varied in the same way as in a previous experiment.[3] The concentration of nickel(II) complex ions was between 0.01 and 0.1 mol/l. *N,N,N',N'*-tetramethyl-*p*-phenylenediamine hydrochloride (TMPD·HCl) was added to the above solutions in an equal molar ratio to nickel(II) complex ions. Xylene, a mixture of *o*-, *m*-, and *p*-xylene, was also used as a glassy solvent in the case of nickel(II) ethyl xanthate complex, where hydrochloric acid free TMPD was used. Each solution was placed in the sample tube for ESR measurements and immersed in liquid nitrogen. The sample was exposed to UV-light through a quartz lens window of the ESR cavity for 10—60 min. An Ushio mercury lamp UI-501C (500 W) was used as a UV source. In order to suppress short wavelength light, a Corning color filter 7-54 was used which does not transmit UV-light with a wavelength smaller than 230 mμ. In the case of hexaaqua nickel(II) complexes, the effect of temperature during and after UV-exposure was closely checked by examining the relative amount of products. ESR experiments were performed in the temperature range -196 °C to -50 °C.

Results and Discussion

Upon exposure to UV-light the sample turned blue, due to the formation of a TMPD cation radical. At the same time, two ESR signals became observable, one at the position of usual organic radicals, and the other at a few hundred gauss lower field (Fig. 1, 3). The line shape of the former signal suggests that some unidentified organic radicals are superimposed on the TMPD cation radical. By raising the temperature of the sample, the signal intensity decreased, only one signal with a characteristic structure remaining observable above -50 °C. The signal is identical with that of the TMPD cation radical which can be easily produced by adding sodium nitrite or lead tetracetate to a TMPD·HCl solution (Fig. 2). On the other hand, the latter signal can be assigned to a univalent nickel complex ion since the *g*-values are characteristic of the complex ion with d^9 electron configuration.[3] The results suggest

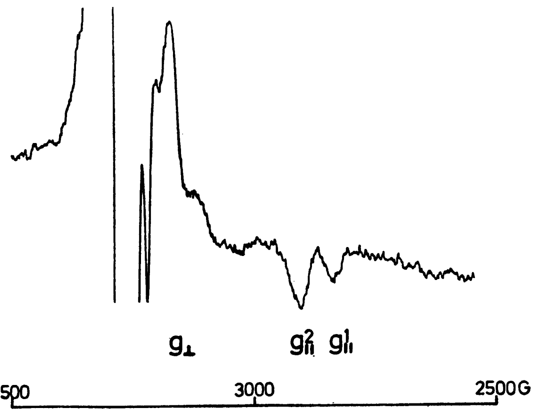

Fig. 1. ESR spectra of $[Ni(bpy)(H_2O)_4]^+$ ($g_{//}^{1}$) and $[Ni(bpy)_2(H_2O)_2]^+$ ($g_{//}^{2}$). $NiCl_2\cdot 6H_2O$: dipy = 1: 1.

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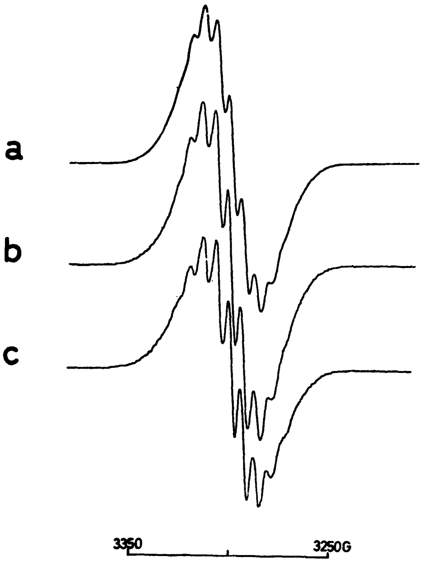

Fig. 2. ESR spectra of TMPD·H^{2+}. a) −196 °C. b) −160 °C. c) −90 °C. The strength is arbitrary.

a possible reaction scheme as follows:

$$\mathrm{TMPD{\cdot}H} + h\nu\ (318\ \mathrm{m\mu}) + h\nu\ (380\ \mathrm{m\mu}) \longrightarrow \mathrm{TMPD{\cdot}H^{2+}} + e^-$$

$$\mathrm{Ni^{2+}\ comp.} + e^- \longrightarrow \mathrm{Ni^{+}\ comp.}$$

$$\mathrm{H_2O\ or\ ethylene\ glycol} + e^- \longrightarrow \mathrm{radicals}$$

The *g*-values of the univalent nickel complex ions are shown in Table 1. By comparing the *g*-values obtained in this experiment with those in the case of γ-irradiation, it can be concluded that the electronic state of the univalent nickel complex ions obtained in both these experiments are identical. This might suggest that the univalent nickel complex ions formed on γ-irradiation are produced by the capture of near-thermal electrons in a later stage of radiation-chemical processes. It seems that TMPD·H$^+$ does not participate in ligation to the nickel(II) ion, and the univalent nickel complex ions retain the ligand molecules originally bonded to the nickel(II) ions. ESR signals of the univalent nickel complex ions disappear above −50 °C and do not appear even if the sample temperature is lowered again.

TABLE 1. ESR PARAMETERS OF NICKEL COMPLEXES

Complexes	Matrices	$g_{//}$	$g_{\perp}$
$[\mathrm{Ni(H_2O)_6}]^+$	EG–H$_2$O	2.468 (2.466)$^{a,b)}$	2.078 (2.076)
$[\mathrm{Ni(H_2O)_6}]^+$	EtOH	2.486 (2.471)	(2.078)
$[\mathrm{Ni(en)(H_2O)_4}]^+$	EG–H$_2$O	2.36$^{c)}$ (2.359)	2.07 (2.072)
$[\mathrm{Ni(en)_2(H_2O)_2}]^+$	EG–H$_2$O	2.29 (2.282)	2.07 (2.064)
$[\mathrm{Ni(bpy)(H_2O)_4}]^+$	EG–H$_2$O	2.32 (2.311)	2.09 (2.075)
$[\mathrm{Ni(bpy)_2(H_2O)_2}]^+$	EG–H$_2$O	2.27 (2.259)	2.09 (2.074)
$[\mathrm{Ni(phen)(H_2O)_4}]^+$	EG–H$_2$O	2.32 (2.317)	2.08 (2.076)
$[\mathrm{Ni(phen)_2(H_2O)_2}]^+$	EG–H$_2$O	2.28 (2.271)	2.08 (2.074)
$[\mathrm{Ni(C_3H_5OS_2)_2}]^-$	Xylene	2.275 (2.280)	2.084 (2.074)
$[\mathrm{Ni(H_2O)_6}]^{3+}$	EG–H$_2$O	2.32 (2.308)	
$[\mathrm{Ni(H_2O)_6}]_2{}^{2+}$	EG–H$_2$O	2.37	2.128

a) ±0.005. b) The *g*-values in parentheses are those obtained in the previous γ-irradiation experiment. c) ±0.01 (for *g*-values with two figures below decimal point).

In a previous experiment on γ-irradiation, an isotropic ESR signal with *g*-value of 2.308 which was tentatively assigned to a tervalent nickel complex ion was observed along with the univalent nickel complex ion having d^9 electron configuration. The isotropic signal observed in the present experiment on UV-light exposure gives the same *g*-value. In order to examine these signals more closely, rigid sample solutions were exposed to UV-light at several temperatures. Between −130 °C and −196 °C, a univalent nickel complex ion with *g*-values of 2.468($g_{//}$) and 2.078($g_{\perp}$) is strong in intensity. This is named low temperature signal. The isotropic signal with *g*-value of 2.308 is weak (Fig. 3). Between −125 °C and −100 C°, a new signal (a high temperature signal) with the *g*-values 2.37($g_{//}$) and 2.128($g_{\perp}$) appears and grows gradually at the expense of the low temperature signal, while the isotropic signal reaches the maximum strength at −115 °C and decays gradually beyond this temperature. The low temperature signal is not observed above −115 °C. In the range −95 °C to −70 °C, only the high temperature signal remains observable. The high temperature signal does not change to the low tempera-

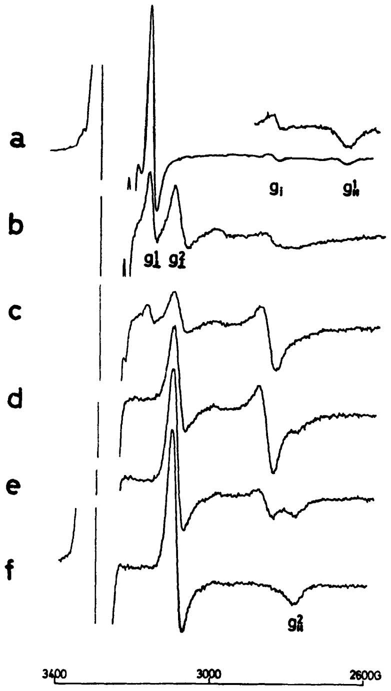

Fig. 3. Three ESR spectra are observed, as the temperature is raised: low temperature signal ($g^1_{//}$ and $g^1_{\perp}$), isotropic signal (g_i), and high temperature signal ($g^2_{//}$ and $g^2_{\perp}$). a) UV-exposure at −140 °C. b) −125 °C. c) −120 °C. d) −115 °C. e) UV-exposed at −115 °C and raised to −100 °C. f) UV-exposed at −115 °C and raised to −90 °C.

ture signal by cooling the rigid solution again to −150 °C, indicating two different chemical species.

The thermal stability of these species is in the order: high temperature signal > isotropic signal > low temperature signal. The low temperature signal and isotropic one are also observed in the previous γ-irradiation experiment. The high temperature signal appears to be due to nickel complex ion because of its relatively large g-shift. A large g-shift, say greater than 0.2, would be most likely caused by strong spin-orbit interaction, and is typical of heavy atoms, *i.e.* nickel ion in this case. From the relation $g_{//} > g_{\perp} > 2$, which is characteristic of a d^9 electron configuration with D_{4h} symmetry elongated along one of the four fold axes of O_h, it can be concluded that the paramagnetic center is due to a univalent nickel complex ion. Since the average g-value $(g_{//}/3 + 2g_{\perp}/3)$ is nearly the same in both low and high temperature signals, these two species do not seem to differ much in electronic state. However, each component of the principal g-values differs a great deal. Copper(II) sulfate does not show one of its principal g-values in any direction in the crystalline state because of the presence of exchange interaction between the neighboring ions in the same unit cell.[4] Thus the apparent g-values differ in the rigid solution state from those in the crystalline state. It appears that the high temperature signal is due to an exchange-coupled dimer of the univalent nickel complex ions.

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