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

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Electron spin resonance has been used to study Ni(I) complex ions produced at 77 K through reduction by γ-irradiation of Ni(II) complexes in glassy solvents. The Ni(I) complex ions give axially symmetrical spectra, suggesting that the Ni(I) ions favor tetragonally elongated octahedral form. From the *g*-values it can be shown that the Ni(I)-to-ligand bonding for different ligands increases in covalency in the order: $H_2O < edta \ll py \sim en \sim xanthate < phen < dipy \ll CN^-$. It can also be shown that the metal-to-ligand bonding of the Ni(I) complex ions is less covalent than that of the corresponding Cu(II) complexes. Measurement of the integrated intensity of the ESR spectrum of $[Ni(I)(H_2O)_6]^+$ with reference to a standard sample of $[Cu(II)(H_2O)_6]^{2+}$ shows that at a total dose of 1×10^6 R the yield of the Ni(I) species is $0.21\pm0.04\%$ of the host complex $[Ni(II)(H_2O)_6]^{2+}$. In addition to the anisotropic spectra of the Ni(I) complex ions, isotropic spectra have been observed in several cases, which are probably due to Ni(III) complex ions. Isotropic feature of these spectra may be explained in terms of dynamic Jahn-Teller effect involving the Ni(III) complex ions.

Metal ions of complexes in solids and in rigid solutions are often reduced by X- or γ-irradiation.[1–4] It has also been reported that oxidation of metal ions occurs in some cases.[5] With the gain or loss of an electron these complexes presumably change immediately in configuration of ligands to take structures with fairly long life-time, which give, in some cases, anomalous optical and ESR spectra.[6,7] For example, several Co(II) complex ions produced through reduction of Co(III) complexes by γ-irradiation have been shown to be in the low spin state ($S=1/2$), in contrast to the usual observation of high spin state ($S=3/2$) of Co(II) complexes.[7]

In a preceding paper, an attempt to produce Ni(I) ions in the host lattice by γ-irradiation of Ni(II) complexes has been reported, where it has been shown that only a few Ni(II) complexes give ESR spectra corresponding to Ni(I) state, and that the electronic structure of Ni(I) ions strongly depends on the host lattices.[8]

The present paper concerns with ESR of Ni(I) complex ions in rigid solutions carrying nitrogen and/or sulfur atoms as donating ones. The *g*-values will be used to discuss the nature of the Ni(I)-to-ligand bonding.

Experimental

Nickel(II) chloride hexahydrate was purified by an anion exchange method to remove a trace amount of cobaltous and cupric ions. Several samples with various molar ratios of nickel(II) ions to ligands were prepared. A mixture of ethylene glycol and water (2: 1 v/v) (EG–H_2O) was used as a glassy solvent. A mixture of *ortho*-, *meta*-, and *para*-xylene was also used as a glassy solvent. The systems studied are listed in Table 1. Degassed sample solutions were immersed

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TABLE 1. NICKEL(II)-LIGAND SYSTEMS EXAMINED

Complex	Matrix	Concn of Ni^{2+}(mol/l)	Molar ratios of Ni^{2+} to ligand
Ni(II)-py	EG–H_2O	0.1	1:0, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:12
Ni(II)-en	EG–H_2O	0.1	1:0, 1:0.5, 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:4, 1:6
Ni(II)-dipy	EG–H_2O	0.1	1:0, 1:0.5, 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:4, 1:6
Ni(II)-phen	EG–H_2O	0.1	1:0, 1:0.5, 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:4, 1:6
Ni(II)-edta	EG–H_2O	0.1	1:0, 1:0.25, 1:0.5, 1:1
Ni(II)-CN^-	EG–H_2O	0.1	1:4
$[Ni(II)(H_2O)_6]Cl_2$	EtOH	0.1	
$[Ni(C_2H_3OS_2)_2]$	Xylene	0.005[a]	
$[Ni(C_3H_5OS_2)_2]$	Xylene	0.01	
$[Ni(C_7H_6O_2N)_2]$	Xylene	0.004[a]	
$[Ni(C_8H_8ON)_2]$	Xylene	0.006[a]	
$[Ni(C_9H_{10}ON)_2]$	Xylene	0.01	
$[Ni(C_{10}H_{12}ON)_2]$	Xylene	0.01	

EG=ethylene glycol, py=pyridine, en=ethylenediamine, dipy=α,α'-dipyridyl, phen=1,10-phenanthroline, $C_2H_3OS_2$= methyl xanthate, $C_3H_5OS_2$=ethyl xanthate, $C_7H_6O_2N$=salicylaldoxime, C_8H_8ON=*N*-methylsalicylaldimine, $C_9H_{10}ON$= *N*-ethylsalicylaldimine, $C_{10}H_{12}ON$=*N*-propylsalicylaldimine.

a) Saturated solution

TABLE 2. ESR PARAMETERS OF NICKEL(I) COMPLEX IONS

Complex ion	Matrix	$g_{//}(\pm 0.002)$	$g_\perp(\pm 0.002)$	$k(10^{-4}\,cm^{-1})$	$k'(10^{-4}\,cm^{-1})$
$[Ni(I)(H_2O)_6]^+$	EG–H_2O	2.466	2.076	0.96	0.63
$[Ni(I)(H_2O)_6]^+$	EtOH	2.471	2.078	0.97	0.64
$[Ni(I)(py)(H_2O)_5]^+$	EG–H_2O	2.402	2.073	0.83	0.60
$[Ni(I)(py)_2(H_2O)_4]^+$	EG–H_2O	2.344	2.071	0.72	0.59
$[Ni(I)(py)_3(H_2O)_3]^+$	EG–H_2O	2.316	2.071	0.65	0.59
$[Ni(I)(py)_4(H_2O)_2]^+$	EG–H_2O	2.282	2.068	0.58	0.56
$[Ni(I)(en)(H_2O)_4]^+$	EG–H_2O	2.359	2.072	0.74	0.59
$[Ni(I)(en)_2(H_2O)_2]^+$	EG–H_2O	2.282	2.064	0.58	0.53
$[Ni(I)(phen)(H_2O)_4]^+$	EG–H_2O	2.317	2.076	0.65	0.63
$[Ni(I)(phen)_2(H_2O)_2]^+$	EG–H_2O	2.271	2.078	0.56	0.64
$[Ni(I)(dipy)(H_2O)_4]^+$	EG–H_2O	2.311	2.075	0.64	0.62
$[Ni(I)(dipy)_2(H_2O)_2]^+$	EG–H_2O	2.259	2.074	0.53	0.61
$[Ni(I)(edta)(H_2O)]^{3-}$	EG–H_2O	2.414	2.077	0.86	0.64
$[Ni(I)(CN)_4]^{3-}$	EG–H_2O	2.131	2.030	0.27	0.25
$[Ni(I)(C_2H_3OS_2)_2]^-$	Xylene	2.282	2.076	0.58	0.63
$[Ni(I)(C_3H_5OS_2)_2]^-$	Xylene	2.280	2.074	0.58	0.61
$[Ni(I)(C_7H_6O_2N)_2]^-$	Xylene	2.250[a]		0.52	
$[Ni(I)(C_8H_8ON)_2]^-$	Xylene	2.311[a]		0.64	
$[Ni(I)(C_9H_{10}ON)_2]^-$	Xylene	2.317[a]		0.65	
$[Ni(I)(C_{10}H_{12}ON)_2]^-$	Xylene	2.317[a]		0.65	

a) Rhombic ESR patterns

in liquid nitrogen and given at 77 K a γ-ray dosage of 1×10^6 R from ^{60}Co source with the dose rate of 5×10^4 R/h. ESR spectra were recorded at 77 K on a JEOL 3BSX spectrometer.

The yield of $[Ni(I)(H_2O)_6]^+$ was determined by comparing the integrated ESR intensity of Ni(I) complex ions with that of a standard sample which contained 6.02×10^{16} ions of $[Cu(II)(H_2O)_6]^{2+}$ in EG–H_2O.[9] The samples used in the present experiment contain 6.02×10^{18} ions of $[Ni(II)(H_2O)_6]^{2+}$ and the concentration of $[Ni(II)(H_2O)_6]^{2+}$ is 1.00×10^{-1} mol/l.

Results and Discussion

In all systems examined, the *g*-tensors are nearly axially symmetric. Since ^{61}Ni, only isotope with nonzero nuclear spin, has a very low natural abundance (1.25%), hyperfine structure due to nickel nuclei was not observed. Principal values of the *g*-tensor ($g_{//}$ and $g_\perp$) were obtained as usual, and the results are summarized in Table 2.

The yield of $[Ni(I)(H_2O)_6]^+$ was found to be 0.21 ± 0.04% of the amount of the host $[Ni(II)(H_2O)_6]^{2+}$ at a γ-ray dosage of 1×10^6 R.[10]

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[9] Since $[Cu(II)\ (H_2O)_6]^{2+}$ and $[Ni(I)\ (H_2O)_6]^+$ are almost the same with respect to the anisotropy of the *g*-tensor($g_{//}=2.400$, $g_\perp=2.099$ for Cu(II) and $g_{//}=2.466$, $g_\perp=2.076$ for Ni(I)), the ESR transition probability, and hence, the integrated intensity is assumed equal to each other between these two complexes.

[10] This corresponds to a *G*-value in radiation chemistry of 0.21 ± 0.04.

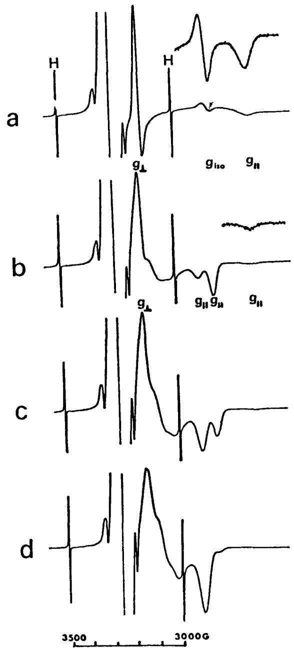

Fig. 1. γ-Irradiated Ni(II)-dipy complexes in rigid ethylene glycol–water solution.
a) Ni^{2+}: dipy=1:0 b) 1:0.5 c) 1:1 d) 1:2

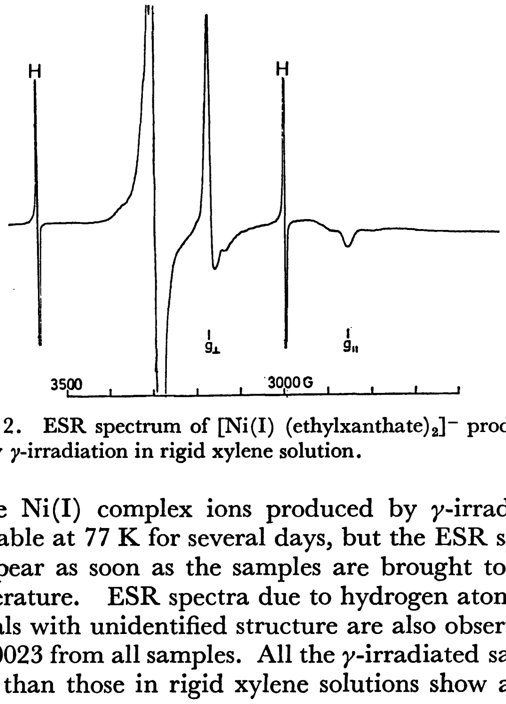

Fig. 2. ESR spectrum of $[Ni(I)\ (ethylxanthate)_2]^-$ produced by γ-irradiation in rigid xylene solution.

The Ni(I) complex ions produced by γ-irradiation are stable at 77 K for several days, but the ESR spectra disappear as soon as the samples are brought to room temperature. ESR spectra due to hydrogen atoms and radicals with unidentified structure are also observed at $g\sim 2.0023$ from all samples. All the γ-irradiated samples other than those in rigid xylene solutions show a deep blue color, which is probably due to solvated electrons.

Assignment of ESR Spectra. Experimental results in Table 2 show that $g_{/\!/}>g_\perp>g_e$ $(=2.0023)$, and that the $g_{/\!/}$-values are strongly dependent on the kind of ligands. It is also noted that g-shifts $(\Delta g=g_{obs}-2.0023)$ are fairly large. The large g-shifts eliminate a possibility that these signals are due to radicals by the solvent and/or ligands. The relation of $g_{/\!/}$, $g_\perp$, and g_e for various electron configurations and multiplets predicted by the ligand field theory is summarized in Table 3. High spin state $(S=3/2)$ of d^7 electron configuration is eliminated from Table 3, since the observed spectra do not show the nature of high spin state. Complex ions with high spin state should have a spin-lattice relaxation time too short to permit the observation of ESR spectra at 77 K and, even if observed, should have large g-values of 4 or 6 by the contribution of orbital magnetic moment. The g-values in Table 3 have been calculated according to the framework of strong field approximation; cubic field, electron-electron repulsion and tetragonal field are successively applied as perturbations. Actually, we have built multiplet wavefunctions taking electron-electron repulsion into consideration to the first order, which are expressed as the linear combinations of seven electron wavefunctions of determinantal type. For instance, for the wavefunctions belonging to the ground state of ^2E_g we have

$$|{}^2E_g\ 1/2\ u\rangle = |d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}d_{xy}\overline{d_{xy}}d_{3z^2-r^2}|$$
$$|{}^2E_g\ 1/2\ v\rangle = |d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}d_{xy}\overline{d_{xy}}d_{x^2-y^2}|$$

All the multiplet wavefunctions are the eigenfunctions of spin-operators, S^2 and S_z, and are transformed in similar fashion with the bases of irreducible representations of O_h group. Tetragonal field is taken into account to the first order. Taking spin-orbit interaction $(H_{so}=\sum_{i=1}^{7}\xi(\vec{r}_i)\vec{l}_i\vec{s}_i)$ and Zeeman interaction $(H_z=\sum_{i=1}^{7}\beta(\vec{l}_i+2\vec{s}_i)\vec{H})$ as perturbation, the second order energy is calculated within forty functions belonging to the ground and the one electron excited configurations. Although the results in Table 3 are obtained by using a simple crystal field theory, these relations should remain unchanged even if configuration interaction is taken into account in an LCAO MO formalism. As Table 3 shows, case A and case D are consistent with the experimental results. As far as we know, complex ions with the d^7 electron configuration have always been shown to be in the $^2A_{1g}$ state (case C), and a

TABLE 3. PREDICTED g-VALUES FOR FOUR DIFFERENT CASES

Case	Config	Multiplet	$g_{/\!/}$	$g_\perp$	Order
A	d^9	$^2B_{1g}$	$2+8\zeta/E(^2B_{2g})^{a)}$	$2+2\zeta/E(^2E_g)$	$g_{/\!/}>g_\perp>2$
B	d^9	$^2A_{1g}$	2	$2+6\zeta/E(^2E_g)$	$g_\perp>g_{/\!/}=2$
C	d^7	$^2A_{1g}$	2	$2+(3+6a_1b_1)\zeta/E(^2E_g{}^a)$ $+(3+6a_2b_2)\zeta/E(^2E_g{}^b)$	$g_\perp>g_{/\!/}=2$
D	d^7	$^2B_{1g}$	$2+(4+8a_1b_1)\zeta/E(^2B_{2g}{}^a)^{b,c)}$ $+(4+8a_2b_2)\zeta/E(^2B_{2g}{}^b)$	$2+(1+2a_1b_1)\zeta/E(^2E^a)$ $+(1+2a_2b_2)\zeta/E(^2E_g{}^b)$	$g_{/\!/}>g_\perp>2$

a) Energy value when that of the ground multiplet is zero.

b) $a_1=-10B/\{(4B+C+A)^2+100B^2\}^{1/2}$, $b_1=(4B+C+A)/\{(4B+C+A)^2+100B^2\}^{1/2}$, $a_2=-10B/\{(4B+C-A)^2+100B^2\}^{1/2}$, $b_2=(4B+C-A)/\{(4B+C-A)^2+100B^2\}^{1/2}$; $A\equiv(116B^2+8BC+C^2)^{1/2}$.

c) $a_1b_1\sim -0.36$, $a_2b_2\sim 0.36$; $B=1115\ cm^{-1}$, $C=5450\ cm^{-1}$ for Ni^{3+}.

TABLE 4. ESR PARAMETERS OF COPPER(II) COMPLEXES

Complex ion	Matrix	$g_{//}$	$g_{\perp}$	k	k'	Ref.
$[Cu(II)(H_2O)_6]^{2+}$	Glycerin–H_2O	2.400	2.099	0.60	0.60	a)
$[Cu(II)(py)_4]^{2+}$	H_2O	2.22		0.33		b)
$[Cu(II)(en)(H_2O)_4]^{2+}$	Glycerin–H_2O	2.281	2.058	0.42	0.34	a)
$[Cu(II)(en)_2(H_2O)_2]^{2+}$	Glycerin–H_2O	2.209	2.047	0.31	0.27	a)
$[Cu(II)(phen)_2]^{2+}$	H_2O	2.280		0.42		c)
$[Cu(II)(dipy)_2]^{2+}$	H_2O	2.270		0.40		c)
$[Cu(II)(CN)_4]^{2-}$	MeOH	2.160	2.033	0.24	0.20	d)
$[Cu(II)(C_7H_6O_2N)_2]$	EtOH, $CHCl_3$–Toluene	2.171	2.020	0.25	0.11	e, f)

a) W. S. Lewis, M. Alei, and L. O. Morgan, *J. Chem. Phys.*, **45**, 4003 (1966).
b) K. Wüthrith, *Helv. Chim. Acta*, **49**, 1400 (1966).
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d) A. Longo and T. Buch, *Inorg. Chem.*, **6**, 556 (1967).
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f) H. R. Gersman and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1961).

d^7 electron configuration in the $^2B_{1g}$ state (case D) has not yet been proved to exist.[11–14] In view of these result, it may be concluded that the observed signals are due to Ni(I) complex ions having the $3d^9$ electron configuration in the $^2B_{1g}$ state (case A).

Structure of Ni(I) Complex Ions. The ESR spectrum shows that $[Ni(I)(H_2O)_6]^+$ has a tetragonally elongated octahedral form, while the host $[Ni(II)(H_2O)_6]^{2+}$ is known to have a regular octahedral form. The lowering of symmetry which is accompanied with the reduction of Ni(II) to Ni(I) is probably due to the Jahn-Teller effect; the ground state of $[Ni(I)(H_2O)_6]^+$ in O_h symmetry would be orbitally degenerate E_g, which is expected to suffer from Jahn-Teller distortion.

Ni(I) Ion-to-ligand Bonding. It has been shown that in a ligand field with D_{4h} symmetry, $g_{//}$ and $g_{\perp}$ for the d^9 electron configuration with $^2B_{1g}$ ground state are given by[15,16]

$$g_{//} = 2.0023 + 8\zeta_0\alpha\beta_1[\alpha\beta_1 - \alpha'\beta_1 S - \alpha'(1-\beta_1^2)^{1/2}T(n)/2]/\Delta E_{xy} \tag{1a}$$

$$g_{\perp} = 2.0023 + 2\zeta_0\alpha\beta[\alpha\beta - \alpha'\beta S - \alpha'(1-\beta^2)^{1/2}T(n)/2^{1/2}]/\Delta E_{xz} \tag{1b}$$

where α and α' are the coefficients for the B_{1g} antibonding orbital, β and $(1-\beta^2)^{1/2}$ are those for E_g, β_1 and $(1-\beta_1^2)^{1/2}$ are for B_{2g}; and ΔE_{xy} and ΔE_{xz} are energy separations between $^2B_{2g}$ and $^2B_{1g}$ and between ^2E_g and $^2B_{1g}$ respectively. Although the Ni(I) complex ions are most probably six-coordinated, Eqs. (1a) and (1b) will be used in the present study by making an assumption that overlap between orbitals of the fifth and sixth ligands and those of the Ni(I) ion is small. Following parameters k and k' represent the degree of delocalization of the 3d electrons of the nickel ion, and may be used as a measure of covalency in the Ni(I) complex ions.[16]

$$k = \alpha\beta_1[\alpha\beta_1 - \alpha'\beta_1 S - \alpha'(1-\beta_1^2)^{1/2}T(n)/2]/\Delta E_{xy} \tag{2a}$$

$$k' = \alpha\beta[\alpha\beta - \alpha'\beta S - \alpha'(1-\beta^2)^{1/2}T(n)/2^{1/2}]/\Delta E_{xz} \tag{2b}$$

It can be seen from Table 2 that the covalency increases in the order: H_2O (0.96) < edta (0.86) ≪ py (0.58) ~ en (0.58) ~ xanthate (0.58) < phen (0.56) < dipy (0.53) ≪ CN^- (0.27). The numbers in parentheses represent parameters k. This order is in agreement with that obtained for Cu(II) complexes (Table 4), well-known spectrochemical series.[17]

In the following the parameter k obtained for the Ni(I) complex ions are compared with those for the corresponding Cu(II) complexes:[18]

$[Ni(I)(H_2O)_6]^+$ (0.96) < $[Cu(II)(H_2O)_6]^{2+}$ (0.60)
$[Ni(I)(en)_2(H_2O)_2]^+$ (0.58) < $[Cu(en)_2(H_2O)_2]^{2+}$ (0.31)
$[Ni(I)(CN)_4]^{3-}$ (0.27) < $[Cu(II)(CN)_4]^{2-}$ (0.24)

In all these cases, the nature of the Ni(I) ion-to-ligand bonding appears to be less covalent than in the case of corresponding Cu(II) ions.

Isotropic Spectra. γ-Irradiated samples containing $[Ni(II)(H_2O)_6]^{2+}$ or $[Ni(II)(edta)(H_2O)]^{2-}$ give additional isotropic spectra. In the cases of $[Ni(II)(en)_3]^{2+}$, $[Ni(II)(phen)_3]^{2+}$ and $[Ni(II)(dipy)_3]^{2+}$ only the isotropic spectra were observed. As in the case of the Ni(I) ions discussed above, the g-shifts are fairly large and are sensitive to the kinds of ligands. These signals

TABLE 5. ESR PARAMETERS OF Ni(III) COMPLEXES

Complex ion	Matrix	$g_{iso}^{a)}$ (±0.01)	$H_{msl}^{b)}$ (G)
$[Ni(III)(H_2O)_6]^{3+}$	EG–H_2O	2.308	37
$[Ni(III)(H_2O)_6]^{3+}$	EtOH	2.309	35
$[Ni(III)(edta)(H_2O)]^-$	EG–H_2O	2.252	67
$[Ni(III)(en)_3]^{3+}$	EG–H_2O	2.204	47
$[Ni(III)(phen)_3]^{3+}$	EG–H_2O	2.196	45
$[Ni(III)(dipy)_3]^{3+}$	EG–H_2O	2.186	45

a) Isotropic g-value b) Maximum slope line width

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[17] B. A. Goodmen and J. B. Raynor, "Electron Spin Resonance of Transition Metal Complexes," *Adv. Trans. Metal. Chem.*, **13**, 135 (1971).

[18] In calculation of k and k', ζ_0=605 cm^{-1} (Ni^+) and ζ_0=830 cm^{-1} (Cu^{2+}) were used.[19]

[19] T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

observed at liquid nitrogen temperature disappear irreversibly when the samples are brought to room temperature.

If the isotropic feature of these spectra comes from dynamic Jahn-Teller effect of the Ni(I) complex ions, the *g*-values should be equal to $(g_{//}+2g_{\perp})/3$. This relation obviously does not hold for $[Ni(I)(H_2O)_6]^+$ and $[Ni(I)(edta)(H_2O)]^{3-}$. Anisotropic *g*-values, $g_{//}$ and $g_{\perp}$, estimated from this relation are too large for $[Ni(I)(en)_3]^+$, $[Ni(I)(phen)_3]^+$, and $[Ni(I)(dipy)_3]^+$ ($g_{//}\sim 2.4$, $g_{\perp}\sim 2.1$).

Another possibility is that the Ni(II) complexes are oxidized to produce Ni(III). Complex ions with d^7 configuration would have ^2E_g ground state in a strong ligand field with O_h symmetry. Since an orbitally degenerate E state has to be split by the Jahn-Teller effect, complexes with d^7 electron configuration would be lower in symmetry than O_h, and hence give anisotropic *g*-tensors. In the case of the dynamic Jahn-Teller effect, isotropic *g*-tensors would be observed. In some d^7 complexes, isotropic *g*-values have been reported, where the results were interpreted in terms of the dynamic Jahn-Teller effect.[13,14]

The high spin state ($S=3/2$) of d^7 complexes would have a spin-lattice relaxation time too short to permit observation of ESR spectra at 77 K and would not show the *g*-value of 2 which is observed in the present case.

In view of the above results it may be concluded that a Ni(III) species is produced along with Ni(I) species by γ-irradiation and that the dynamic Jahn-Teller effect is responsible for the isotropic feature of the ESR spectra.

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