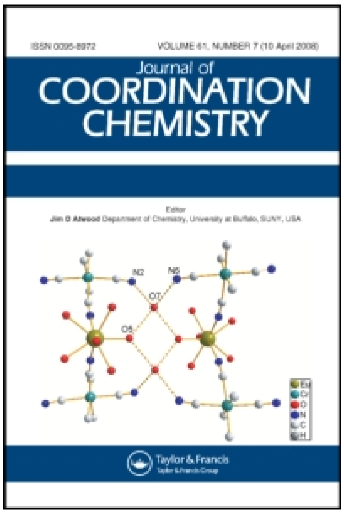

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ELECTRON SPIN RESONANCE OF γ-IRRADIATED COBALT(III) COMPLEXES; ELECTRONIC AND SPIN STATES OF HOT COBALT(II) IONS

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ESR investigation of the γ-ray irradiated Co(III) complexes have been carried out. The identification and the classification of the irradiation products on the basis of the ESR signal patterns, and the electronic and the spin states of the products are discussed.

Co(III) complexes are reduced by the γ irradiation into Co(II) complexes, where the produced Co(II) ions have low spin configurations, $S = 1/2$. Authors refer to these particular spin states as hot ions.

It has been reported that divalent cobalt ion, Co(II), is produced by the radiochemical reactions of Co(III) complexes[1,2]. However, further investigation on the electronic and the spin states of the products has not been given, and, accordingly, direct evidence of the formation of Co(II) or more detailed information on the electronic states of the latter has not been obtained. This paper shows the results of ESR investigation on the γ-ray irradiated Co(III) complexes, where the identification and the classification of the irradiation products are fulfilled. The electronic and the spin states of the products are also discussed.

ESR is capable to determine the spin states of Co(II) ions whether they are in the high spin configuration of $(t_{2g})^5(e_g)^2$, $S = 3/2$, or in the low spin configuration of $(t_{2g})^6(e_g)^1$, $S = 1/2$. [3,4] Complex of high spin state as the aquocomplex, $[Co(H_2O)_6]^{2+}$, has a short relaxation time, and prevents observation of the ESR spectrum except at very low temperature.[5,6] Whereas, the complex of low spin state such as hexacyano Co(II) complex gives ESR spectrum even at room and liq.N_2 temperatures as the consequence of the long relaxation time.[7]

In the present investigation, sixty seven cobalt complexes have been irradiated, because Co(III) complexes include a wide variety of complexes which cover the whole spectroscopic series, and moreover, the ESR patterns of the Co(II) ions are simple if they take the low spin states.

The Co(II) ions which are investigated in this work will be referred to as the hot ions. Fujiwara and Nakamura has proved with respect to the single crystal of Pd(II) acetylacetonate that this type of hot Pd(I) ions are produced by γ-irradiation.[8] We assume that this situation similarly holds with respect to the cases of Co(III) complexes. The ESR spectra of the complexes which are investigated in the present work are classified into eight groups as it will be shown in the text. Moreover, it has been found that many of the products take low spin state. The latter fact will particularly be noted here as the opposite to the expectation according to the ligand field effects of the ligands.

EXPERIMENTAL

All samples of Co(III) complexes were irradiated by Co-60 γ-rays at room or liquid nitrogen temperatures at a dose rate of about $1 \sim 5 \times 10^5$ R/hr. The amount of the total dose is about 1.5×10^6 R, and the irradiation has been given in the air or in 10^{-3} mmHg atmosphere. All ESR measurements were carried out at liquid nitrogen temperature. The samples irradiated at liquid nitrogen temperature were first measured at liquid nitrogen temperature, and, then, after leaving them for several hours at room temperature, measured again at liquid nitrogen temperature. Some samples showed no difference between the two measurements, whereas some other did show the difference. With the latter samples, temperature dependence of the ESR spectra was examined. The JEOL 3BS X-band spectrometer with 100 KHz modulation was used for the ESR measurements.

RESULTS

The dose rate and the magnitude of the total dose have shown no sizable effects with respect to the ESR patterns. Due to the incompleteness of degassing, the degassing effect will not be discussed in detail. However, two groups of samples, one degassed to 10^{-3} mmHg and the other not, both have shown almost comparable ESR figures, except that the former shows a little smaller line width.

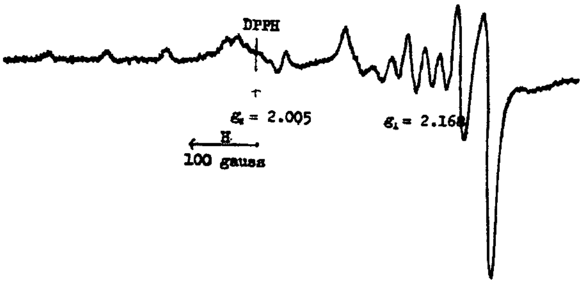

FIGURE 1 The typical ESR spectrum of γ irradiated Co(III) complexes in Group A; ESR spectrum of the γ irradiated $K_3[Co(CN)_6]$ at 77° K. The spectre of Group C is overlapped near the field of DPPH.

With the samples except $K_3[Co(CN)_6]$, $K_3[Co(CN)_5X](X = Cl, Br, NO_2)$ and $[Co(NH_3)_5X]X_2$ ($X = Cl, Br$), no sizable effect was observed with respect to the temperature during irradiation. The results of these complexes will be published later.

The Co(III) complexes γ-irradiated at room temperature in the air give several kinds of ESR spectra as shown in Figures 1 to 7. It should be noticed that they show completely different line shapes. As mentioned before, the γ-irradiated complexes can be classified into eight groups on the basis of the patterns of the observed ESR spectra of the paramagnetic irradiation products. Figures 1, 2, 3, 4, 5, 6 and 7 correspond to the ESR spectra of the γ-irradiated Co(III) complexes in the groups A, B, C, D, E, F and H, respectively. Some complexes which show two kinds of ESR signals are listed in two entries of groups.

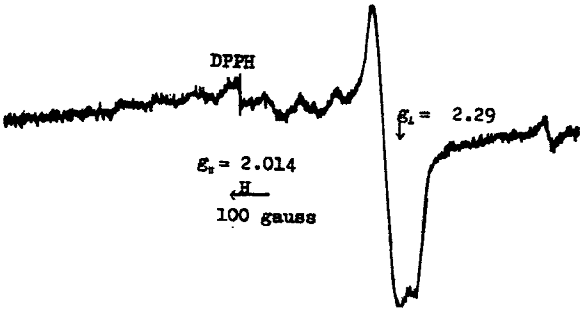

FIGURE 2 The typical ESR spectrum of the γ irradiated Co(III) complexes in Group B at 77° K; the signal of radical is overlapped.

TABLE I

Group A

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (gauss)	$A_{\perp}$ (gauss)	P (cm^{-1})	κ (cm^{-1})	P/P_0 (%)
$K_3[Co(CN)_6]$	2·005	2·168	90	27·3	0·018	0·077	70.4
$K_3[Co(CN)_5NO_2]$	2·005	2·170	88·3	27·1	0.017	0·056	66·1
$K_3[Co(CN)_5Cl]$	2·008	2·178	92·2	29·1	0·018	0·056	70·8
$K_3[Co(CN)_5Br]$	2·003	2·170	90·5	25	0·017	0·056	66·1

TABLE II

Group B

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (gauss)	A_N (gauss)
$[Co(en)_2(CN)_2](NO_3)$	2.011	2.32	65	12
$NH_4[Coen(NH_3)_2(SO_3)_2]$	2.014	2.29	92	
$[Co(NH_3)_4(SO_3)CN]$	2.017	2.34	92	

TABLE III

Group C

Complex	$g_{//}$	$g_{\perp}$	$A_{//}$ (gauss)	$A_{\perp}$ (gauss)	P (cm^{-1})	κ (cm^{-1})	P/P_0 (%)
$K_3[Co(CN)_5Cl]$	2.007	1.998	14.6	8.2	0.0026	−0.02	10
$K_3[Co(CN)_5Br]$	2.017	1.997	14.2	8.0	0.0025	−0.02	10
$[Coen_2(CN)_2]NO_3$	2.06	1.99					
$[Co(NH_3)_6](NO_3)_3$	2.082	1.993	18.3	9.7	0.0032	0	12
$[Co(NH_3)_5NO_2](NO_3)_2$	2.078	1.994	18.2	9.5	0.0031	0	12
$[Co(NH_3)_5NO_3](NO_3)_2$	2.081	1.995	17.7	12.2	0.0034	0.05	13
$[Co(NH_3)_5OH](NO_3)_2$	2.079	1.993	16.0	8.3	0.0028	0	11
$[Co(en)_3]Cl_3 \cdot H_2O$	2.086	2.004	17.8	9.1			
$[CotetrenCl]ZnCl_4$	2.091	1.99	17.5	—			
$[Co(NH_3)_4(CO_3)](NO_3)$							
$[Co(NH_3)_4CO_3]_2(SO_4)_3$							
$NH_4[Co(NH_3)_4(SO_3)_2]$							

Group D

$[Co(NH_3)_4CO_3]\ (NO_3)$

TABLE IV

Group E

Complex	$g_{//}$	$g_{\perp}$	$A_{//}$ (gauss)
$[Co(NH_3)_6](NO_3)_3$	2.017	2.01	56.7
$[Co(NH_3)_6]_2(SO_4)_3$	2.016	2.01	61.3
$[Co(NH_3)_6]Cl_3$	—[a]	—	—
$[Co(NH_3)_6]_2(C_2O_4)_3$	—	—	—
$[Co(NH_3)_5NCS]VO_3$	1.982	2.02	67.7
$[Co\ (NH_3)_5SO_4]_2(SO_4)$	—	—	—
$[Co(NH_3)_5F](NO_3)_2$	2.013	2.01	75.8
$[Co(NH_3)_4CO_3]_2SO_4$	—	—	—
$[Co(NH_3)_4CO_3]NO_3$	—	—	—
trans $[Co(NH_3)_4Cl_2]Cl$	2.010	2.01	59.3
cis $[Co(NH_3)_4Cl_2]Cl$	2.016	2.07	83.7
cis $[Co(NH_3)_4(OH_2)Cl]Cl_2$	2.012	2.02	73.8
cis $[Co(NH_3)_4(OH_2)_2]Cl_3$	—	—	—
$[Co(NH_3)_3(NO_3)_3]$	1.994	2.01	72.2
$[Codien(NO_2)_3]$	1.998	—	33
$[Co(en)_2Br_2]Br \cdot HBr$	—	—	—

[a] The intensity of signals are weak, so the correct values of them cannot be obtained.

Group F

(i) $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_5Br]Br_2$, $[Co(NH_3)_5(OH_2)]Br_3$,
(ii) $[Co(en)_2CO_3]Cl$, $[Co(en)_2CO_3]NO_3$,
(iii) $[Co(NH_3)_5CN]Cl_2$,
(iv) $[CodienCl_3]$,
(v) $[Co(en)_2(NCS)_2]Cl$

Group G

$[Co(NH_3)_5(OH_2)](ClO_3)_3$, $[Co(NH_3)_5(OH_2)]_2(C_2O_4)_3$, $[Co(NH_3)_5S_2O_3]Cl$, $[Co(NH_3)_5I](NO_3)_2$, $[Co(NH_3)_5CH_3COO](NO_3)_2$, $[Co(NH_3)_4(OH_2)CN]Cl_2$, $[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3$, $[Co(en)_2(OH_2)OH]Br_2$, $[CotrienCl_2]Cl$, cis and trans $[Co(en)_2Cl_2]Cl$, cis $[Co(en)_2Cl_2]Cl \cdot HCl \cdot H_2O$, $[Co(NH_3)_2(C_2O_4)CO_3]H_2O$, $K[Co(NH_3)_2(C_2O_4)_2]H_2O$, $K_3[Co(C_2O_4)_3]$, $[Co(acac)_3]$, $K[Co(edta)]$.

Group H

$Na_3[Co(NO_2)_6]$, $K_3[Co(NO_2)_6]$, $K[Co(NH_3)_2(NO_2)_4]$, $[Co(NH_3)_3(NO_2)_3]$, cis and trans $[Co(NH_3)_4(NO_2)_2](NO_3)$, cis and trans $[Co(en)_2(NO_2)_2](NO_3)$, $[Co(NH_3)_5NO_2]Cl_2$, $[CO(NH_3)_5ONO]Cl_2 \cdot$

Complexes which belong to the group F show various types of signals which cannot be simply interpreted. The compounds in group G do not give any observable ESR signals of Co(II) ions. Complexes of group H which contain NO_2 group as the ligand present the spectra of NO_2 radical by irradiation, however, no signal of Co(II) ions. The g-values and hyperfine coupling constants of the radicals are almost same with respect to all complexes of this group and agree with the values which have been reported in the literatures[9, 10] as shown in Table V.

Following remarks can be deduced from the results with the groups of A, B, C, D, and E, all of which show clear signals of Co(II) ions.

(i) The ESR spectra are interpretable in terms of the spin Hamiltonian for $S = \frac{1}{2}$.

(ii) The g-values and the hyperfine coupling constants are almost same with the complexes which belong to the same group, suggesting that the irradiation products are same or much the same.

(iii) Much difference of the ESR patterns is observed among the different groups. This will suggest that the orbitals which hold the odd electron are much different from each other among the groups.

TABLE V

ESR parameters of NO_2 radical in various states.

	irrad. Co(III)complexes with NO_2 ligands.[a]	irrad. $NaNO_2$[b]	NO_2 adsorbed on ZnO[c]	MgO[c]
g_x	2.006	2.0057	2.007	2.005
g_y	1.993	1.9910	1.994	1.9915
g_z	2.002	2.0015	2.003	2.002
A_x*	149.4	138.4	146.1	148.8
A_y*	135.4	130.9	132.0	136.7
A_z*	192.0	190.2	181.1	189.0
$A_{iso.}$*	158.9	153.2	153.1	158.2

* MHz/sec.
[a] this work.
[b] Z. Heldes and R. Livingston, *J. Chem. Phys.* **35**, 563 (1961).
[c] R. D. Iyengar and V. V. Subba Rao, *J. Am. Chem. Soc.* **90**, 3267 (1968).

DISCUSSION

A. *Identification of the Irradiation Products*

ESR patterns of Co(II) ions in the low spin state may be interpreted in terms of the spin Hamiltonian of (1),

$$\mathscr{H} = \beta H\cdot\tilde{g}\cdot S + I\cdot\tilde{A}\cdot S \qquad (1)$$

where H is the magnetic field, S, the spin angular momentum, I, the nuclear spin angular momentum, $\tilde{g}$, the g-tensor, $\tilde{A}$, the hyperfine coupling constant tensor and β, the Bohr magneton. The g-values and A are calculated theoretically to the 1st order as shown in Table VI, where it is assumed that the odd electron is localized in one of the 3d orbitals of Cobalt.[11, 12] By comparing the observed parameters with the calculated ones, the nature of the paramagnetic irradiation products is discussed following.

Group A: ESR parameters of group A show a relation that $g_{//} \sim g_e$, $g_\perp > g_e$, and $|A_{//}| > |A_\perp|$ as shown in Figure 1. According to Table VI, this relation refers to the fact that the unpaired electron sites mainly in the $3d_{3z^2-r^2}$ orbital of cobalt, and, furthermore, that the electronic distribution has axial symmetry along the elongated Z axis.

Values of P and κ are calculated from the observed A values as shown in Table I. The magnitude of P for the free ion of Co(II), P_o, is taken as 0.0257 cm^{-1} [13] according to the Freeman and Watson's value of $< r^{-3} >$.[14] The value of P/P_o in Table I implies that the unpaired electron is delocalized toward the ligand CN groups and that the metal ligand bonds carry a nature of covalency. It should be noticed that the ESR parameters of the γ-irradiation products of the complexes in the group A definitely refer to the pentacyano Co(II) complex, $[Co(II)(CN)_5]^{3-}$. The Co(II) cyano or isonitrile complexes[7, 15–17] give the spectra of almost same characters of patterns as shown in Table VII. However, the g values and the hyperfine constants A show a clear dependence on the number of the ligand cyano or isonitrile groups. Namely, $g_\perp$ decreases in the order of four-, five-,

TABLE VI

List of the calculated g values and hyperfine coupling constants.

3d orbital	$g_{//}$	$g_\perp$	$A_{//}$ or A_z	$A_\perp$ or $A_{x,y}$	
$d_{x^2-y^2}$	$2[1+4\lambda/\Delta_1]$,	$2[1-\lambda/\Delta_2]$,	$P(-\kappa+2/7)$,	$P(-\kappa-4/7)$	
d_{xz}	very large		$P(-\kappa+2/7)$,	$P(-\kappa+2/7)$,	$P(-\kappa-4/7)$
d_{yz}	very large		$P(-\kappa+2/7)$,	$P(-\kappa-4/7)$,	$P(-\kappa+2/7)$
$d_{3z^2-r^2}$	2 ,	$2[1+\lambda/\Delta_3]$,	$P(-\kappa-2/7)$,	$P(-\kappa+4/7)$	
d_{xy}	$2[1-4\lambda/\Delta_1]$,	$2[1+\lambda/\Delta_4]$,	$P(-\kappa+2/7)$,	$P(-\kappa-4/7)$	

where, $\Delta_1 = |E_{x^2-y^2} - E_{xy}|$, $\Delta_2 = |E_{x^2-y^2} - E_{xz,\,yz}|$,
$\Delta_3 = |E_{3z^2-r^2} - E_{xy,\,yz}|$, $\Delta_4 = |E_{xy} - E_{xz,\,yz}|$, and
$P = 2\beta\beta_n\gamma_{Co}\langle r^{-3}\rangle$.

TABLE VII

ESR parameters of various cyano and isonitril Co(II) complexes.

Complex	Matrix	$g_{//}$	$g_{\perp}$	$A_{//}$**	$A_{\perp}$**	κ	ref.*
$Co(CNR)_6$	RCN	2.005	2.09	64	70	0.196	a
R = Me, Et, $C_6H_{11}\cdot$		2.011	2.1		75		
$Co(MeCN)_5$ + excess RCN		2.025	2.095	65	75		b
$Co(CNMe)_5(MeOH)$		2.00	2.044		74	0.175	a
$Co(CNR)_4Cl_2$		2.00	2.095	65	75	0.208	a
$Co(CN)_5$	ethyleneglicol + water	1.992	2.157	87	28		c
$Co(CN)_5$	solid	1.996	2.177	90	24		d
$Co(CN)_5$	MeOH	2.006	2.157	87.4	28.6	0.046	a
	H_2O	2.005	2.161	88.5	29.8		a
$Co(CNMe)_5$	CH_2Cl	2.0115	2.1227	77.2	59	0.123	a
$Co(CNEt)_5$	CH_2Cl	2.0064	2.1275	80.2	50.3	0.123	a
$Co(CNMe)_5$	ethyleneglicol + water	2.000	2.117	78	57		b
$K_3[Co(CN)_6]$ irrad.	γray	2.005	2.168	90	27	0.077	this work
	X-ray	2.010	2.170 2.167	83.5	26.9 25.2		e
	electron	2.004	2.174	89	25		f

* a; Ref. 15, b; Ref. 16, c; Ref. 7, d; Ref. 18, e; Ref. 11, f; Ref. 19. ** (gauss)

six-cyano or isonitrile complexes, $|A_{//}| < |A_{\perp}|$ for the six-coordinated complex, whereas, $|A_{//}| > |A_{\perp}|$ for the five-coordinated complex. Also, the κ which is obtained by calculation is about 0.2 for the six- and 0.02 ~ 0.1 for the five-coordinated complexes.[15] The observed values of g, A and κ of the γ-irradiation products of group A complexes as shown in Table I refer to the five coordinated cyano complexes, $[Co(CN)_5]^{3-}$.

Pentacyano cobaltous complex, $[Co(CN)_5]^{3-}$, has so far been known by ESR only in solution[15] or in the thermodecomposed solid of the dimer $[Co_2(CN)_{10}]^{-6}$ [18]. ESR has been measured with the X-ray and electron beam irradiation products of $K_3[Co(CN)_6]$ by McDowell *et al.* and Danon *et al.* [11,19] The g-values and the hyperfine coupling constants obtained by these authors are also shown in Table VII. Although their values are slightly different from those obtained in this experiment, all products of γ-ray, X-ray or electron beam irradiation will be assigned to the same species by taking into consideration the polytypism of this complex.[20,21] The irradiation product by electron beam has been assigned to $[Co(CN)_5]^{3-}$ or $[Co(CN)_4]^{2-}$ by Danon *et al.*[19]

Group B: The general features of the ESR spectra of this group are similar to those of the group A except that $A_{\perp}$ is much smaller than that of the group A and that the hyperfine structure of the $g_{\perp}$ part of the spectra is not resolved (Figure 2). The ligand species which form the complexes of this group are CN, SO_3, NH_3, and ethylenediamine, and those which are taken as the strongly coordinating ligands in the spectrochemical series. According to the literatures, similar spectra have been obtained with Co(II)-phthalocyanine complexes, where the odd electron is claimed to be mainly localized in the $3d_{3z^2-r^2}$ orbital.[22,23] Although the values of $g_{//}$ are a little larger than the theoretical value of g_e, the unpaired electron in the compounds of this group is also assumed to be mainly localized in $3d_{3z^2-r^2}$ orbital with a slight distortion of symmetry around Z axis.

With the complexes which contain SO_3 group as ligand a sharp line of $g = 2$ is observed beside the signal of Co(II) ion.

Superhyperfine structure due to two nitrogen atoms is observed in the irradiated $[Co(en)_2(CN)_2](NO_3)$. This suggests that the electron spin interacts with the nitrogen atoms of CN groups (cf. Figure 8).

Group C: The features of the spectra of this group are $g_{//} > g_e \gg g_{\perp}$ and each part of the spectra is resolved into eight hyperfine lines with a hyperfine coupling constant of about 10 gauss (cf. Figure 3). With respect to the ESR features of the values of

g and A, and the line shapes, this signal is very much similar to that obtained in the systems where tetraphenylporphine Co(II) ion[24] or N, N'-ethylenebis(3-methoxysalicylideneiminato)Co(II) ion[25] in pyridine are exposed to oxygen. We assume that the observed ESR signals refer to the complex which is formed by the coordination of oxygen.

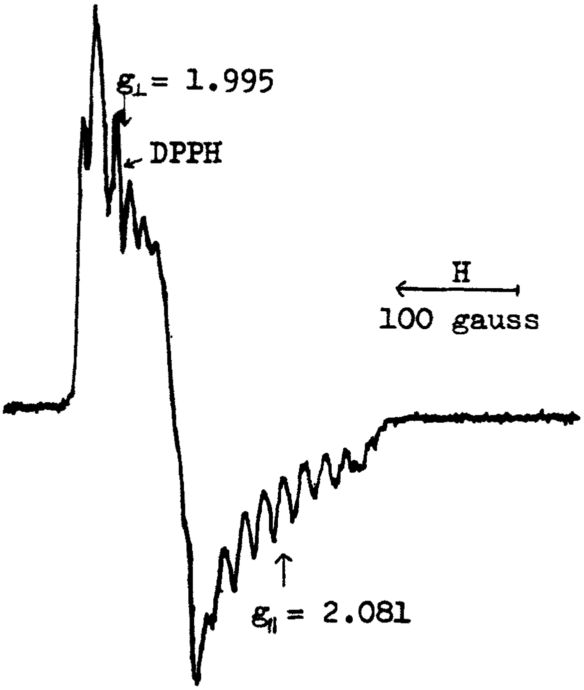

FIGURE 3 The typical ESR spectrum of the γ irradiated Co(III) complexes in Group C at 77° K; ESR spectrum of the γ irradiated [Co(NH$_3$)$_5$NO$_3$](NO$_3$)$_2$.

It is well known that Co(II) cyano or ammine complexes form a dimer structure where oxygen molecule bridges the complexes with a molar ratio of Co to O_2 of 2 to 1.[18, 26–28] Besides this, complex with oxygen in the ratio of 1 to 1 has recently been reported in bis-salicyladehydeimine Co(II) complex,[29, 30] superoxocobalamine,[31] and Co(II) Schiff base compounds.[32] Moreover, adduct, (Co-3-methoxysalicylideneiminato)pyridine$\cdot O_2$, has also been produced.[33] The number of the hyperfine lines in the observed spectra which is sixteen, and not fifteen, refers to the superposition of two sets of eight lines for $g_{//}$ and $g_\perp$ lines. We attribute these spectra to the paramagnetic products of oxocomplexes as shown in Figure 9. Small difference is observed among the complexes of this group in the g-values and the A values. This may be attributed to the difference in the species of the ligand and of the counter ions.

By assuming that the unpaired electron is localized in one of the $3d$ orbitals of cobalt, the ESR parameters may be calculated as shown in Table VI. With the results of the ESR measurements the unpaired electron under consideration occupies $3d_{x^2-y^2}$ orbital. One gets a value of 0.1 for P/P_o. This is a very small value, and it may be taken to imply that the unpaired electron is more dominantly localized in the oxygen orbital. The aforementioned result will imply that the irradiation product is $[\text{Co(III)}\ L_5 - O_2^-]^{2+}$, not $[\text{Co(II)}\ L_5 - O_2]^{2+}$. In accordance with this statement, reference may be referred to which concludes that the unpaired electron in Co orbital is only by 10%.[25]

Group D: The ESR spectra of this group (Figure 4) may be taken as the overlap of two kinds of signals. One is the signal which is the same with that of group C and the other not clear. Consideration of the line shape of this signal implies the presence of a dimer which is bridged by oxygen molecule. Example of the latter has appeared in the literature.[27]

Group E: The ESR signals of this group (Figure 5) are anisotropic, $g// > g_\perp$, and $|A_{//}| > |A_\perp|$. Hyperfine structure of the $g_\perp$ part is overlapped with that of $g_{//}$ part. Moreover $g_\perp$ part is split into x and y directions. The correct values of g or those of the hfs coupling constants cannot be obtained by the simple observation of the spectra.

The similar signals as that of Figure 5 have been obtained with maleonitriledithiolate Co(II) complexes, in which cobalt is coordinated with four S

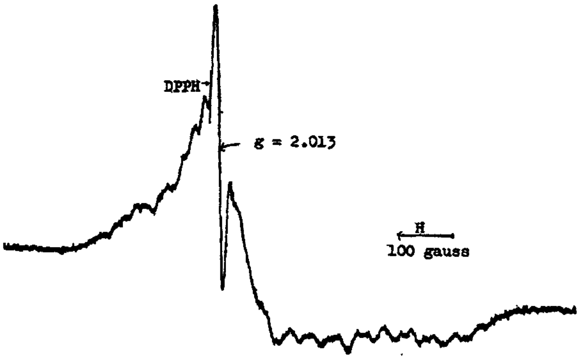

FIGURE 4 The typical ESR spectrum of the γ irradiated Co(III) complexes in Group D at 77° K; ESR spectrum of the γ irradiated [Co(NH$_3$)$_5$CO$_3$](NO$_3$).

atoms of square planar[34] or with a complex of a square pyramidal with one P and four S atoms.[12] In the latter cases, the unpaired electron has been assigned to occupy d_{xy} and d_{yz} orbitals. In all cases of the compounds of this group the paramagnetic irradiation products are assumed to be heavily distorted from the octahedral symmetry of the starting materials.

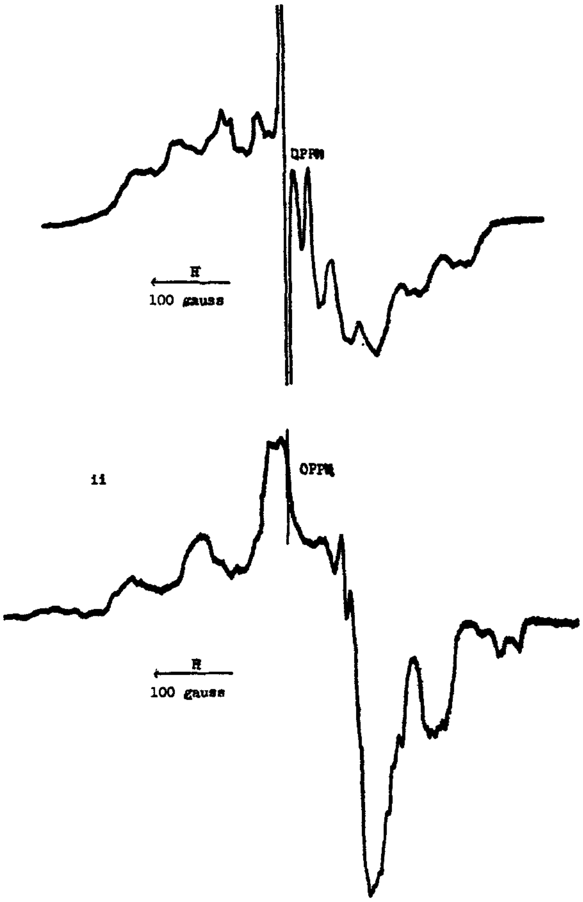

FIGURE 5 The typical ESR spectra of the γ irradiated Co(III) complexes in Group E at 77° K; ESR spectra of the γ irradiated: (i) $[Co(NH_3)_6]_2(SO_4)_3$ and (ii) *cis* $[Co(NH_3)_4Cl_2]Cl$.

The ESR signals in F group are attributed to Co(II) ion, however, further detailed analysis of the spectra is not given as the result of the uncompleteness of the spectra.

Similarly, as the patterns of the spectra of G and H groups are not clear, that detailed discussion will be postponed until further clear-cut experimental results are obtained.

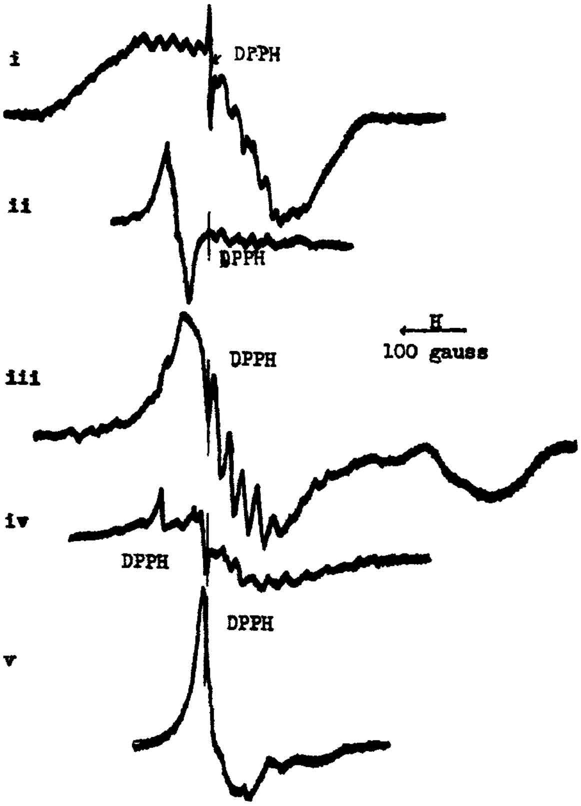

FIGURE 6 The typical ESR spectra of the γ irradiated Co(III) complexes in Group E at 77° K; ESR spectra of the γ irradiated: (i) $[Co(NH_3)_5Cl_2]Cl_2$, (ii) $[Co(en)_2CO_3]Cl$, (iii) $[Co(NH_3)_5CN]Cl_2$, (iv) $[CodienCl_3]$ and (v) $[Co(en)_2(NCS)_2]Cl$.

B. Electronic and Spin States of the Irradiation Products.

In A, it has been shown that the γ-irradiated complexes give the spectra of Co(II) ions, and, furthermore, that the patterns of the spectra can be classified into several groups. As it has also been mentioned in A, we assume that the γ-produced Co(II) ions site in the same crystal field of the same ligands as before the irradiation. Hence, deep interest is called upon seeing the correlation between the patterns and the optical data which refer the crystal field strengths. A typical result of this examination is as shown in Figure 10, where the horizontal line refers to the frequency of the absorption band of the host compound and the vertical to the codes of classification. The Co(III) complexes in the righter side in the horizontal scale are those which are coordinated with the ligands of stronger crystal field. We will add here that the ESR signals of

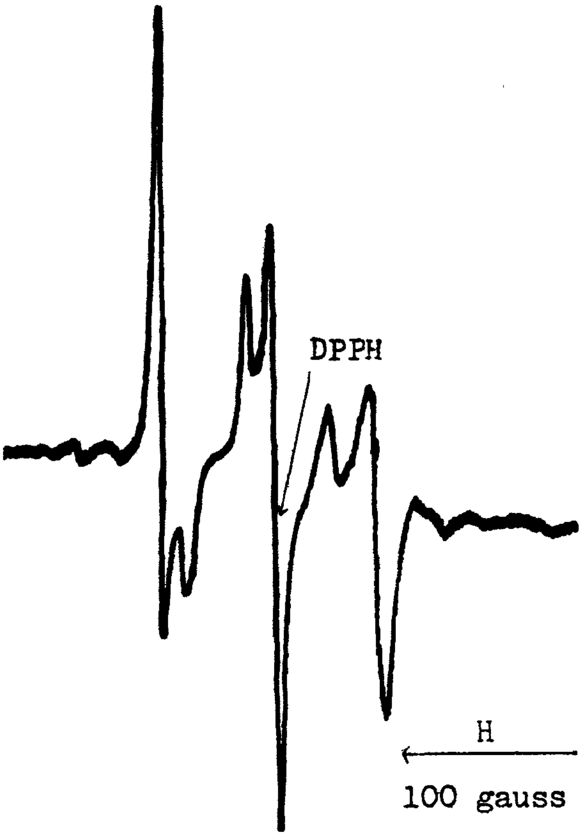

FIGURE 7 ESR spectre of NO_2 radical at 77° K produced by the γ irradiation of the Co(III) complexes with NO_2 groups as the ligand.

Co(III) ions in the irradiation products show a tendency of lower stability in the order from A to G.

Following are deduced from this figure.

(i) Co(III) complexes which have larger splitting of 3*d* orbitals, give clearer ESR signal and the lifetime of the signal is long.

(ii) The Co(III) complexes which have the upper ligands in the spectrochemical series such as CN, and SO_3 give the signal of large anistrophy. (examples; A and B groups).

(iii) Oxocomplex (C, D groups) of Co(II) is produced only by Co(III) complexes whose maximum frequency of the first absorption band lies in the range of $59 \sim 60 \times 10^{13}$ sec $^{-1}$. This may imply that the crystal field energy is not much different between the oxocomples and the complexes of C and D groups which carry oxygen atoms as ligands.

(iv) It is difficult to obtain ESR signals of Co(II) ions from Co(III) complexes of polydentate ligands such as ethylenediamine, ethlenediamintetraaceti-acid, acetylaceton and oxalic acid, even if the ligand field splitting is large enough to make low spin state of Co(II) ion.

(v) Most of Co(III) complexes which belong to F and G groups contain the weaker ligands in the lower spectroscopic series, and clear cut ESR spectrum of Co(II) ion is not observed.

These experimental facts conclusively refer that the stability of the low spin state of Co(II) which is produced by γ-irradiation in the Co(III) complexes much depends on the magnitudes of the d-d splittings of Co(III) complexes before irradiation. This will suggest furthermore that one electron enters into the lowest empty energy level of Co(III) complex on the reduction of central metal ion by γ-irradiation. The Co(III) ions in the original complexes have six 3*d* electrons and lower three orbitals are occupied. Upon reduction, another electron enters one of the orbitals and the Co(II) ion is formed in a low spin configuration, $(d\gamma)^6(d\epsilon)^1$. In order that this configuration is stable, d-d splitting must be large. So, in the groups A and B, more stable and strong ESR signals are observed. In Co(III) complexes with a weak ligand field, the clear-cut ESR signals of Co(II) ions are not

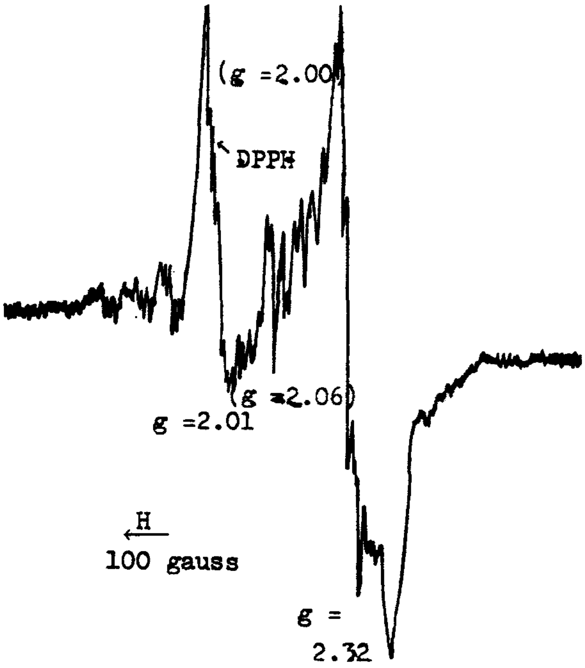

FIGURE 8 ESR spectre of γ-irradiated $[Co(en)_2(CN)_2]Cl$ at 77° K. Both the signal corresponding to the Group B and the signal corresponding to the Group C are overlapped. The former spectrum shows five hyperfine structure due to the two CN groups in the g_{11} part.

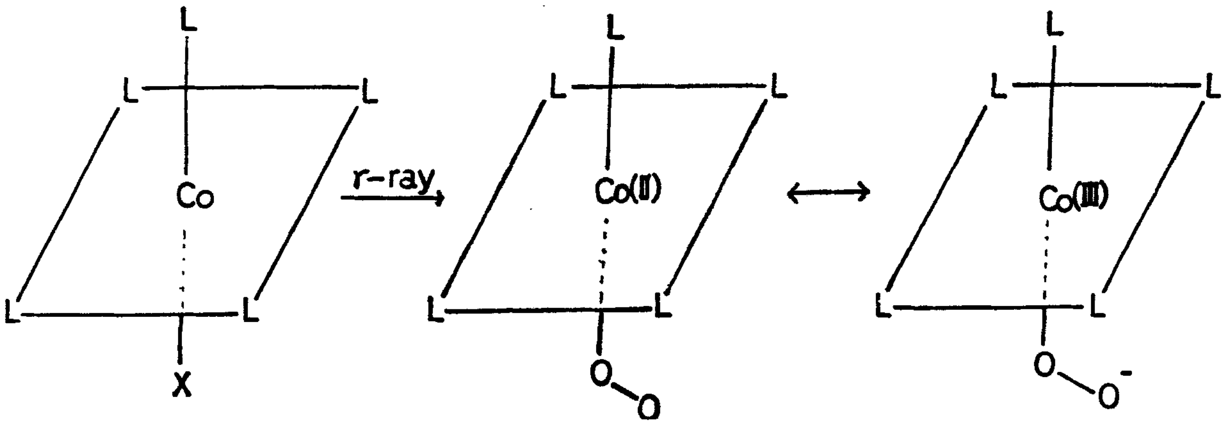

FIGURE 9 Cobalt oxocomplex with the 1 : 1 ratio of Co(III) to O_2, which is produced by the γ-irradiation of Co(III) complexes in Group C. L refers to the ligand such as CN, NH_3, en and tetren.

observed because the spin state changes into the Co(II) high spin configuration.

As mentioned before, ESR signal of Co(II) ion has not been observed in Co(III) chelate complexes. This may be due to the instability of the products of the γ-ray reduction or due to the weakened ligand field which is caused by the destruction of ligands. In the oxalato Co(III) complexes, the latter may be referred to as responsible, because, according to the results of radiolysis, G(Co^{2+}) values of them are very large in comparison to the other ammine Co(III) complexes.[1, 35]

Co(II) complexes which are obtained by the γ-irradiation of the compounds of A, B, C, D and E groups take low spin configurations as shown above. This is not in accord with the general understanding that all ligand which form the complexes of A, B, C, D, E groups except CN group, should produce weak field for Co(II) ion, accordingly, Co(II) ion of high spin configuration.[3, 4] The observed results of the present experiment may be interpreted in terms of the fact that the Co(II) ions of γ-irradiation products site in the crystal field of low spin Co(III) even if the central cobalt atom has been reduced by irradiation. This interpretation may get plausible if one thinks of the slowness of the reaction rate between the Co(III) and Co(II) ions.[4] The reaction rate of Co(III) of low spin state to Co(II) high spin is generally very slow even in solution. The difference of the ionic radius between two ions may be counted as one of the sources of this fact.[4] As it will be seen in Table VIII, the metal-ligand bond lengths in the Co(II)-L complexes are much larger than those of Co(III)-L ones. Although the change of the bond length must be accompanied with the usual reduction of Co(III) ions, this will not hold with respect to the present situation where the small amount of Co(II) complexes site in the rigid host lattice of Co(III) complexes.

Thus, the rate of the reaction from Co(III) ion of low spin state to Co(II) ion of high spin state should be very small in comparison to that of the solutional system. The γ-produced Co(II) ions of low spin state may be in a transient state between Co(III) low spin state and Co(II) high spin state, changing only the valence without the corresponding change of the metal-ligand bond lengths. The stability of the present hot Co(II) ions must be related with the ionic radius of Co(II) ions. With

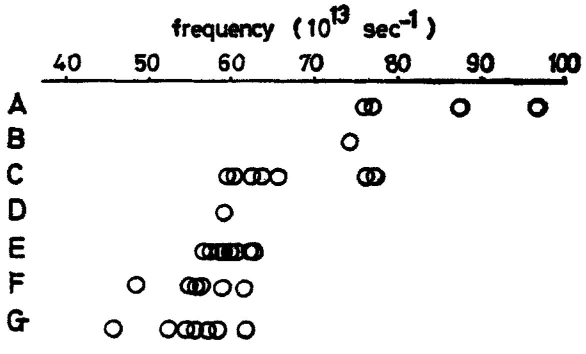

FIGURE 10 The correlation of the irradiation products (ESR spectra) to the frequencies of the maximum of the first absorption bands of Co(III) complexes before irradiation. The horizontal line shows the frequency and the vertical one shows the various kinds of spectra in the order of the stability of the signal.

TABLE VIII

Bond lengths of Co-L in the Co(II) and Co(III) complexes.

	Co(II) ion		Co(III) ion	
Ligand	Bond length (A)	Complex	Bond length (A)	Complex
C			2.00 2.07	$Co(CN)_6$
N	1.99	$Copy_4Cl_2$	1.91	$Co(NH_3)_5Cl$
	2.11	$Co(NH_3)_6$	1.96	$Co(NH_3)_6$
			2.00	$Co(en)_2Br_2$
O	1.90	Co(edta)		
	2.23	$Co(acac)_2(OH_2)_2$	1.91	$Co(acac)_2(OH_2)_2$
Cl	2.32	$Co(py)_4Cl_2$	1.97	$Co(NH_3)_3(OH_2)Cl_2$
	2.43	$CoCl_2(OH_2)_4$	2.30	$Co(NH_3)_5Cl$

respect to the latter problem, more detailed investigation is now being carried out and the results will be reported elsewhere.

The decay of the ESR signal of Co(II) is, of course, proceeded. Two processes are possible; one, the change from the low spin state to the high spin state of Co(II) and the other, oxydization toCo(III) low spin. The latter could be the main process of the decay actually, as the decay gets faster by contact with air or by warming, even shaking by hand.

CONCLUSION

ESR spectra of sixty-seven kinds of γ-irradiated Co(III) complexes were observed at liq. N_2 temperature. They showed several kinds of line shapes which are classified clearly. The ESR spectra can be interpreted in terms of the spin Hamiltonian of $S = 1/2$ and $I = 7/2$. This refers that Co(III) complexes are reduced to Co(II) complexes of low spin configuration by γ-irradiation.

The paramagnetic irradiation products are determined on the basis of the ESR line shapes. $[Co(CN)_5]^{3-}$ ions are produced from cyano complexes which have strong ligand field. The unpaired electron is delocalized in the $3d_{3z^2-r^2}$ orbital of cobalt and the ligand orbital with covalency. Co(III) complexes which have the oxygen rich ligands or oxygen rich counter ions (for example, NO_2, NO_3, OH, OH_2, CO_3, SO_4, etc.), form the oxocomplexes in the ratio of $Co/O_2 = 1/1$, $[Co(III)\ X_5 - O_2^-]$. In the latter, the unpaired electron is localized mainly in O_2^- orbital and about 10 percent is present in Co $3d_{x^2-y^2}$ orbital.

In the case of Co(III) complexes in the E group the unpaired electron is localized in Co $3d_{xy}$ or d_{yz} orbitals and these complexes are strongly distorted from the octahedral symmetry of the starting complexes. The paramagnetic irradiation products cannot clearly be determined.

Clear signals are not obtained from Co(III) complexes with weak ligands and chelate complexes. As a whole, Co(II) complexes of low spin configuration are produced by the γ-irradiation of Co(III) complexes which are the transient unstable ones in the sense that they occupy the site of the rigid Co(III) complexes, changing the valence state only from Co(III) to Co(II) without corresponding change of the ligand fiels.

Authors refer these particulars state of spins as hot ions.

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