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Mössbauer Studies of the Gamma-ray-irradiation Effects of 1,10-Phenanthroline Compounds

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Mössbauer and infrared spectroscopies have been applied to the study of the gamma-ray-irradiation effects on eleven iron 1,10-phenanthroline compounds: $[Fe(phen)_2X_2]$ ($X=Cl^-$, $HCOO^-$, NCO^-, $\frac{1}{2}Ox^{2-}$, $\frac{1}{2}Mal^{2-}$, CN^-, and NO_2^-), $[Fe(phen)_3]X_2\cdot nH_2O$ ($X=Cl^-$, ClO_4^-, $HCOO^-$, and NO_2^-), $[Fe(phns)_2](ClO_4)_2\cdot 2H_2O$ and $[Fe(phnc)_2](ClO_4)_2\cdot H_2O$ (phen = 1,10-phenanthroline, phns = 1,10-phenantroline-2-carbothioamide, and phnc = 1,10-phenantroline-2-carboxamide). For all the low-spin complexes except $[Fe(phen)_3](HCOO)_2\cdot 6H_2O$, no chemical changes were observed on the Mössbauer spectra after irradiation. All the iron(II) complexes in the high-spin state except $[Fe(phen)_2Cl_2]$ and $[Fe(phnc)_2](ClO_4)_2\cdot H_2O$ were, however, changed to iron(III) species under the influence of irradiation. Three iron(II) complexes in the intermediate-spin state were sensitive to gamma-rays.

A large number of investigations have been carried out by means of Mössbauer spectroscopy into the gamma-ray-irradiation effects on various compounds. Friedt and Danon have reported that the principal effect of the radiolysis in iron(III) chelates could be interpreted in terms of the H radicals originating from the decomposition of the ligands, which had a high mobility and a high reducing property.[1] In iron(III) potassium oxalate, the reduction from iron (III) to iron(II) species by gamma-ray irradiation has been observed.[2] The primary process of this change is a charge transfer from the ligand to the iron, and the new oxidation state is stabilized by the destruction of the complex with an evolution of gases. In the emission Mössbauer spectroscopic study, the relation between the radiosensitivity and the degree of conjugation of the ligand has been elucidated.[3] The higher degree of conjugation a molecule possesses, the lower the probability of the radiolysis of its molecule.

In this work, in order to clarify the relationship of the radiation effect between the ligand field's strength (or the bond character) and the oxidation number (or the ground state of the iron complex), we synthesized several iron complexes with 1,10-phenanthroline and other related compounds as the ligands. The chemical changes which occurred in these complexes upon gamma-ray irradiation were investigated through Mössbauer spectroscopy. The following iron complexes were used; they were prepared according to the methods described in the literature: $[Fe(phen)_3]X_2\cdot nH_2O$ ($X=ClO_4^-$, $HCOO^-$, and NO_2^-)[4] $[Fe(phen)_2(CN)_2]$,[5] $[Fe(phen)_2(NO_2)_2]\cdot 1/2H_2O$,[6] $[Fe(phen)_2X_2]$ ($X=Cl^-$, $HCOO^-$, and NCO^-),[7] $[Fe(phen)_2X_2]\cdot nH_2O$ (X = 1/2 oxalate, 1/2 malonate, and F^-),[8] $[Fe(phnc)_2](ClO_4)_2\cdot H_2O$,[9] and $[Fe(phns)_2](ClO_4)_2\cdot 2H_2O$.[10]

Experimental

The analytical data of the complexes prepared are listed in Table 1. The microanalyses were carried out at the Elemental Analysis Center of Kyushu University.

All the samples were sealed in glass tubes under a vacuum and were irradiated at a dose rate of 8.7×10^5 Rh^{-1} in a cylindrical tube of a 3500 Ci cobalt-60 unit of Kyushu University. All the irradiations were done at room temperature. The samples were kept at the temperature of

Table 1. Analytical data of the iron complexes

Complex	Calcd (%)			Found (%)			μ_{eff} (B.M.)
	C	H	N	C	H	N	
$[Fe(phen)_3](ClO_4)_2$	54.36	3.40	10.57	53.47	3.11	10.46	
$[Fe(phen)_3]Cl_2\cdot 5H_2O$	57.08	4.52	11.10	57.56	4.36	11.11	
$[Fe(phen)_3](NO_2)_2\cdot 5H_2O$	55.53	4.40	14.39	55.92	4.28	14.07	
$[Fe(phen)_3](HCOO)_2\cdot 6H_2O$	57.44	4.82	10.57	56.87	4.52	10.39	
$[Fe(phen)_2(NO_2)_2]\cdot 1/2H_2O$	55.73	3.11	16.24	55.24	3.18	15.84	
$[Fe(phen)_2(CN)_2]$	66.68	3.44	17.94	66.53	3.37	17.85	
$[Fe(phns)_2](ClO_4)_2\cdot 2H_2O$	40.58	2.88	10.92	40.32	3.00	10.30	
$[Fe(phen)_2Ox]\cdot 3H_2O$	55.39	3.97	10.03	55.70	3.66	9.62	3.8
$[Fe(phen)_2Mal]\cdot 3H_2O$	56.60	4.23	9.79	56.07	4.34	9.88	3.2
$[Fe(phen)_2F_2]\cdot 4H_2O$	54.76	4.59	10.64	55.25	4.84	10.72	2.8
$[Fe(phen)_2Cl_2]$	59.17	3·11	11.50	58.12	3.40	11.39	
$[Fe(phen)_2(HCOO)_2]$	61.58	3.58	11.07	61.54	3.60	11.19	
$[Fe(phen)_2(NCO)_2]$	62.41	3.22	16.80	62.38	3.23	16.86	
$[Fe(phnc)_2](ClO_4)_2\cdot H_2O$	43.41	2.80	11.68	43.20	2.77	11.50	
$[Fe(phen)_3](ClO_4)_3\cdot 2H_2O$	46.08	2.94	9.03	46.45	3.03	9.03	
$[Fe(phen)_2Cl_2](ClO_4)$	48.98	2.70	9.56	49.14	2.75	9.55	

liquid nitrogen from the end of the exposure to the start of the measurement of the Mössbauer and the infrared spectra in order to protect the radiation effect of the samples from thermal annealing. The total radiation dose was 1.0×10^9 R or 5.8×10^8 R.

A gas-chromatographic study was carried out under the conditions to be described below, by using a G-8 type apparatus of the Yanagimoto Co., Ltd. The sensing element consisted of thermal conductivity cells and the potentiometer was operated at 90 mV. The temperature of the conductivity cell block and the column 10 feet long were kept at the same temperature, either 40 or 170 °C. Gaseous products of the irradiated $[Fe(phen)_2(HCOO)_2]$ were injected directly by using a syringe connected to the carrier-gas-inlet line. Helium was used as the carrier gas at a flow rate of about 15 ml min^{-1}, while active carbon was used as the stationary phase.

The Mössbauer spectra of the unirradiated and irradiated samples were obtained at the temperature of liquid nitrogen using a constant-acceleration spectrometer made by Austin Science Associates. The data were stored in a 1024-channel analyser, type 5200 (Ino-tec, Inc). A 5-mCi cobalt-57 diffused into a Pd foil was used as the source. The isomer shift was calibrated relative to the center of the spectrum of an iron foil at 293 K. All the spectra were fitted to the Lorentzian line shape using the least-squares method.

The infrared spectra were obtained by using a Hitachi Grating Infrared Spectrophotometer, type 215, in the region from 650 to 4000 cm^{-1}. The KBr disk was used for the sample preparation.

Results and Discussion

Figures 1—7 show the Mössbauer absorption spectra of the unirradiated and irradiated samples: $[Fe(phen)_3](ClO_4)_3\cdot2H_2O$, $[Fe(phen)_3](HCOO)_2\cdot6H_2O$, $[Fe(phen)_2(HCOO)_2]$, $[Fe(phen)_2(NCO)_2]$, $[Fe(phen)_2Ox]\cdot3H_2O$, $[Fe(phen)_2Mal]\cdot3H_2O$, and $[Fe(phen)_2F_2]\cdot4H_2O$. The Mössbauer parameters before and after irradiation for all the samples are listed in Tables 2—5.

No chemical changes were observed in the Mössbauer spectra of $[Fe(phen)_3](ClO_4)_2$, $[Fe(phen)_3]Cl_2\cdot5H_2O$, $[Fe(phen)_2Cl_2]$, $[Fe(phnc)_2](ClO_4)_2\cdot H_2O$, $[Fe(phns)_2](ClO_4)_2\cdot2H_2O$, and $[Fe(phen)_2Cl_2](ClO_4)$. From these observations, it can be supposed that the radicals produced by the decomposition of 1,10-phenanthroline upon irradiation contribute to indetectable changes in the iron(II) ground state. On the other hand, the low-spin $[Fe(phen)_3](ClO_4)_3\cdot2H_2O$ was reduced to the low-spin iron(II) (55%) species. It is clearly observed that the high-spin complex $[Fe(phen)_2Cl_2](ClO_4)$ is not sensitive to radiation. This may indicate that the irradiation effect in this case depends upon the difference in the ground state of the iron atom, and the reduction from iron(III) to iron(II) species results from the electron transfer from the ligand to the central metal. $[Fe(phns)_2](ClO_4)_2\cdot2H_2O$ and $[Fe(phnc)_2](ClO_4)_2\cdot H_2O$, for which we could not detect any irradiation effect, are in high-spin and low-spin respectively. The difference between the ligands of

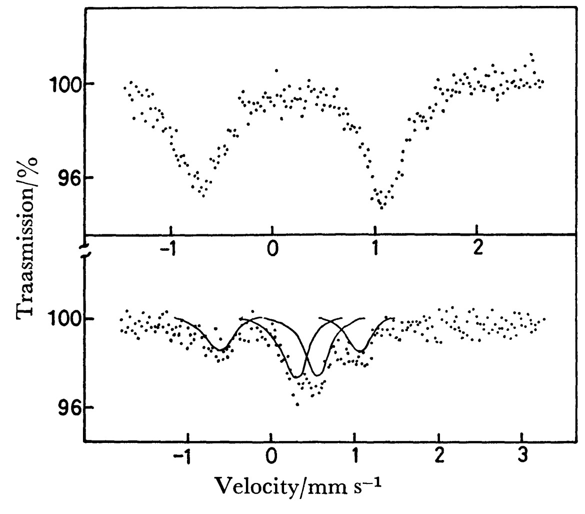

Fig. 1. Mössbauer spectra at 80 K of (a) non-irradiated and (b) irradiated $[Fe(phen)_3](ClO_4)_3\cdot2H_2O$.

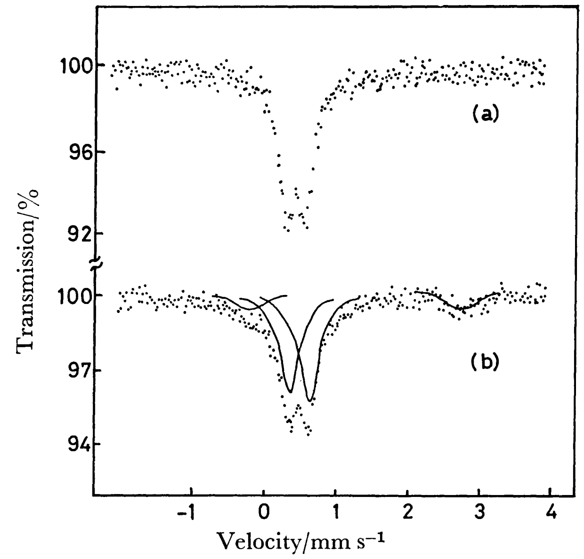

Fig. 2. Mössbauer spectra at 80 K of (a) non-irradiated and (b) irradiated $[Fe(phen)_3](HCOO)_2\cdot6H_2O$.

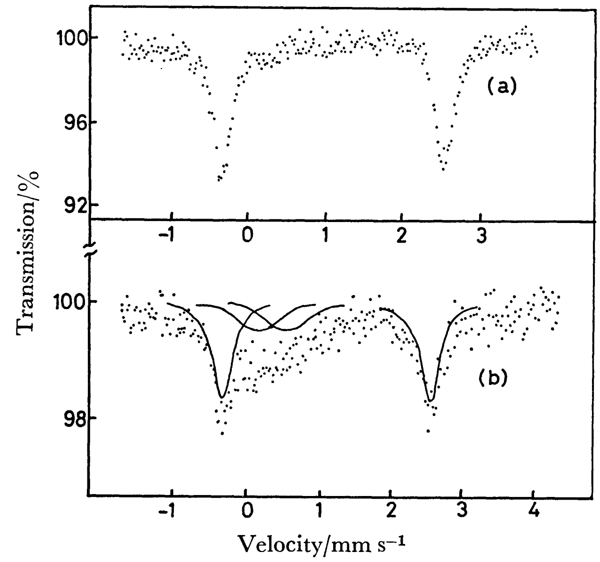

Fig. 3. Mössbauer spectra at 80 K of (a) non-irradiated and (b) irradiated $[Fe(phen)_2(HCOO)_2]$.

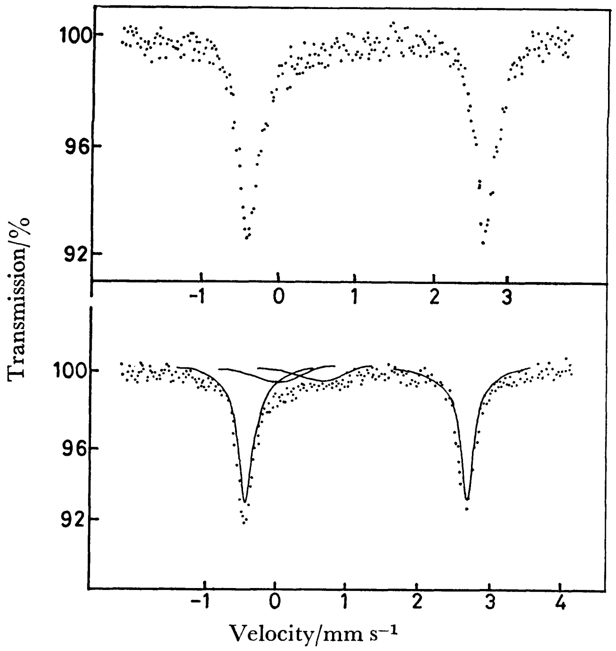

Fig. 4. Mössbauer spectra at 80 K of (a) non-irradiated and (b) irradiated [Fe(phen)$_2$(NCO)$_2$].

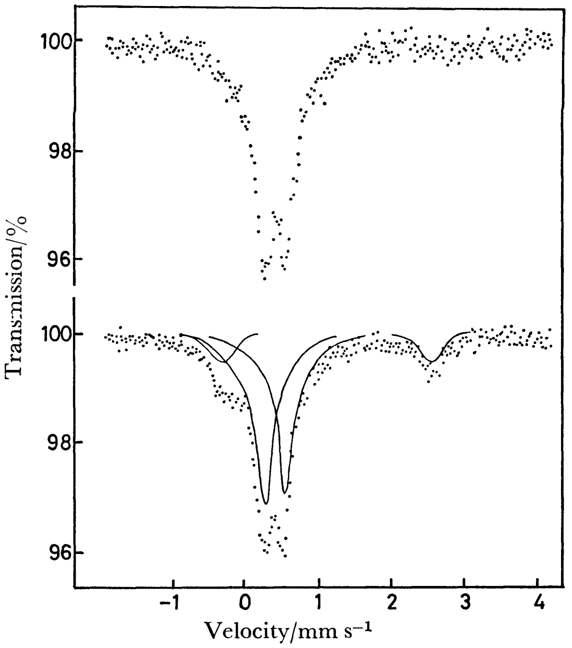

Fig. 6. Mössbauer spectra at 80 K of (a) non-irradiated and (b) irradiated [Fe(phen)$_2$Mal]·3H$_2$O.

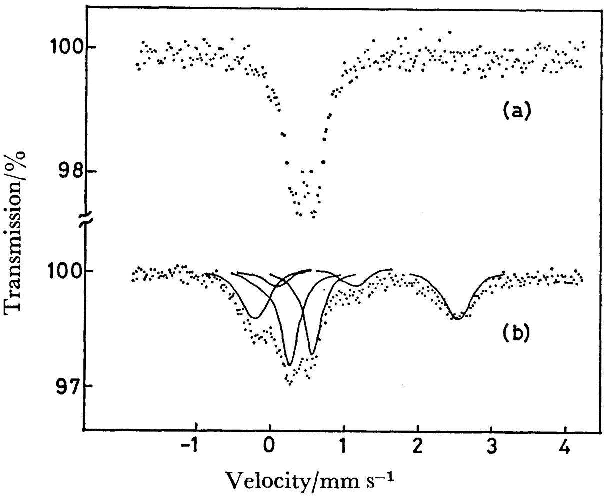

Fig. 5. Mössbauer spectra at 80 K of (a) non-irradiated and (b) irradiated [Fe(phen)$_2$Ox]·3H$_2$O.

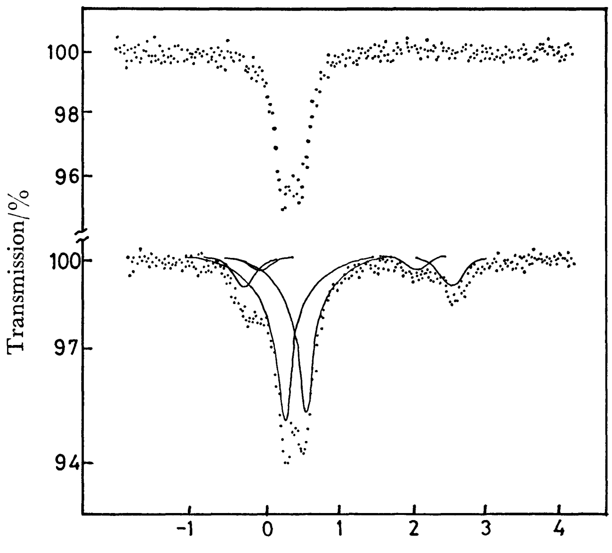

Fig. 7. Mössbauer spectra at 80 K of (a) non-irradiated and (b) irradiated [Fe(phen)$_2$F$_2$]·4H$_2$O.

the two samples is only that of carbonyl and thionyl groups, which were presumed to be sensitive to gamma-ray irradiation. It may be supposed that, even if the ligands are excited by gamma-rays, the decomposition of the ligands is suppressed because of the highly conjugated π-bond of the ligands.

Gütlich *et al.* have reported that high- and low-spin iron(II) species were observed in the emission spectra of [^{57}Co(phen)$_3$](ClO$_4$)$_2$.$^{11)}$ The appearance of the high-spin iron(II) ion does not agree with the results of our external-irradiation experiment.

New peaks attributable to high-spin iron(II) species in the [Fe(phen)$_3$](HCOO)$_2$·6H$_2$O and to high-spin iron(III) species in the [Fe(phen)$_2$(HCOO)$_2$] and [Fe(phen)$_2$(NCO)$_2$] appeared after the exposure to gamma-rays. There may be a possibility that the new peaks attributable to low-spin iron(II) species are hidden in the absorption band of the high-spin iron(III) species, because their line widths are too broad to be resolved. However, we can not confirm the existence of the overlapping because of the technical difficulty in the curve fitting. The yield of high-spin iron(II) species produced in the irradiated [Fe(phen)$_3$](HCOO)$_2$·6H$_2$O was 15%, while those of the high-spin iron(III) species in [Fe(phen)$_2$(HCOO)$_2$] and [Fe(phen)$_2$(NCO)$_2$] were 43% and 18% respectively. The small values of the isomer shift of iron(III) species in the above two samples suggest that there are four or five coordinated species with 1,10-phenanthroline as a result of the elimination of formate and isocyanate ions by gamma-ray irradiation. A gas-chromatograph-

TABLE 2. MÖSSBAUER PARAMETERS OF THE SAMPLES BEFORE AND AFTER γ-RAY IRRADIATION MEASURED AT 80 K

Complex	Exp. $\times 10^8$R	δ[a] / $\mathrm{mm\ s^{-1}}$	Δ[b] / $\mathrm{mm\ s^{-1}}$	Γ[c] / $\mathrm{mm\ s^{-1}}$	
$[\mathrm{Fe(phen)_3}](\mathrm{ClO_4})_2$	0	0.38	0.31		
	10.0	0.41	0.31		
$[\mathrm{Fe(phen)_3}]\mathrm{Cl_2\cdot 5H_2O}$	0	0.35	0.26	0.29	0.28
	5.8	0.36	0.25	0.27	0.28
$[\mathrm{Fe(phen)_2Cl_2}]$	0	1.08	3.26		
	10.0	1.12	3.30		
$[\mathrm{Fe(phnc)_2}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$	0	1.11	2.36	0.41	0.41
	10.0	1.12	2.54	0.48	0.48
$[\mathrm{Fe(phns)_2}](\mathrm{ClO_4})_2\cdot 2\mathrm{H_2O}$	0	0.33	0.51	0.29	0.30
	10.0	0.33	0.49	0.29	0.34
$[\mathrm{Fe(phen)_3}](\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	0	0.19	1.80		
	10.0	0.17	1.74		
		0.41	0.28		
$[\mathrm{Fe(phen)_2Cl_2}](\mathrm{ClO_4})$	0	0.40	0		
	10.0	0.33	0		

a) Isomer shift. b) Quadrupole splitting. c) Full width at half-maximum.

TABLE 3. MÖSSBAUER PARAMETERS OF THE SAMPLES BEFORE AND AFTER γ-RAY IRRADIATION MEASURED AT 80 K

Complex	Exp. $\times 10^9$R	δ / $\mathrm{mm\ s^{-1}}$	Δ / $\mathrm{mm\ s^{-1}}$	Γ / $\mathrm{mm\ s^{-1}}$		S / S(total)	SSWR[a] / Freedom
$[\mathrm{Fe(phen)_3}](\mathrm{HCOO})_2\cdot 6\mathrm{H_2O}$	0	0.40	0.26	0.28	0.27		
	1	0.47	0.28	0.32	0.31	85	423/387
		1.26	2.94	0.47	0.35	15	
$[\mathrm{Fe(phen)_2(HCOO)_2}]$	0	1.12	2.90	0.27	0.23		
	1	1.11	2.89	0.34	0.34	57	373/387
		0.29	0.35	0.74	0.74	43	
$[\mathrm{Fe(phen)_2(NCO)_2}]$	0	1.14	3.10	0.33	0.29		
	1	1.13	3.10	0.27	0.27	82	388/391
		0.31	0.56	0.73	0.73	18	

a) SSWR: sum of the squares of the weighted residuals.

TABLE 4. MÖSSBAUER PARAMETERS OF THE SAMPLES BEFORE AND AFTER γ-RAY IRRADIATION MEASURED AT 80 K

Complex	Exp. $\times 10^9$ R	δ / $\mathrm{mm\ s^{-1}}$	Δ / $\mathrm{mm\ s^{-1}}$	Γ / $\mathrm{mm\ s^{-1}}$		S / S(total)	SSWR[a] / Freedom
$[\mathrm{Fe(phen)_2Ox}]\cdot 3\mathrm{H_2O}$	0	0.41	0.27	0.32	0.23		
	1	0.40	0.28	0.32	0.27	46	
		1.15	2.74	0.47	0.47	44	388/391
		0.58	1.06	0.39	0.39	10	
$[\mathrm{Fe(phen)_2Mal}]\cdot 3\mathrm{H_2O}$	0	0.40	0.28	0.30	0.31		
	1	0.41	0.27	0.33	0.30	80	468/389
		1.14	2.84	0.34	0.34	20	
$[\mathrm{Fe(phen)_2F_2}]\cdot 4\mathrm{H_2O}$	0	0.41	0.25	0.27	0.28		
	1	0.41	0.27	0.27	0.29	73	
		1.15	2.86	0.35	0.35	22	405/385
		0.97	2.15	0.27	0.27	5	

TABLE 5. MÖSSBAUER PARAMETERS OF THE SAMPLES BEFORE AND AFTER γ-RAY IRRADIATION MEASURED AT 80 K

Complex	Exp. $\times 10^8$ R	δ / $\mathrm{mm\ s^{-1}}$	Δ / $\mathrm{mm\ s^{-1}}$	Γ / $\mathrm{mm\ s^{-1}}$	
$[\mathrm{Fe(phen)_3}](\mathrm{NO_2})_2\cdot 5\mathrm{H_2O}$	0	0.35	0.27	0.26	0.26
	5.8	0.38	0.26	0.32	0.32
$[\mathrm{Fe(phen)_2(NO_2)_2}]\cdot 1/2\mathrm{H_2O}$	0	0.33	0.43	0.27	0.28
	5.8	0.33	0.41	0.25	0.32
$[\mathrm{Fe(phen)_2(CN)_2}]$	0	0.22	0.60	0.29	0.29
	5.8	0.21	0.60	0.35	0.34

ic study revealed that a large amount of carbon dioxide and a small amount of carbon monoxide existed in the irradiated [Fe(phen)$_2$(HCOO)$_2$]. It is considered that iron(III) species with a four- or five-coordinated structure are formed because of the decomposition of the formate ion. The radicals originating from the decomposition of 1,10-phenanthroline and hydrated waters of the second coordination sphere do not bring about the oxidation of the iron atom, because no irradiation effect was observed in [Fe(phen)$_3$](ClO$_4$)$_2$ and [Fe(phen)$_3$]Cl$_2$·5H$_2$O. The new peaks attributable to the high-spin iron(II) species which appeared in [Fe(phen)$_3$](HCOO)$_2$·6H$_2$O after irradiation suggest that 1,10-phenanthroline has been decomposed by the reaction of 1,10-phenanthroline with some radicals or electrons arising from gamma-ray decomposition of the formate ion. This is true because the low-spin iron(II) state can be attained only in such a coordination situation as when the iron atom is coordinated with three 1,10-phenanthroline molecules. By comparing [Fe(phen)$_3$](HCOO)$_2$·6H$_2$O with [Fe(phen)$_2$(HCOO)$_2$], it may be concluded that the oxidation reaction has occurred only in the latter complex. It is obscure, however, whether this difference is attributable to that in the ground states of the central metals, because we can not ignore the reaction of the iron ion with the decomposition products of the coordinated and uncoordinated HCOO$^-$, or the reaction of H$_2$O with the radicals produced. At present, the real reason why the high-spin iron(III) species appears in [Fe(phen)$_2$(HCOO)$_2$] is ambiguous. The yields of high-spin iron(II) and iron(III) species appearing in [Fe(phen)$_3$[(HCOO)$_2$·6H$_2$O and [Fe(phen)$_2$(HCOO)$_2$] after irradiation were 15% and 43% respectively. This indicates that the radiation effect on the central iron of HCOO$^-$ in the first coordination sphere is about three times as large as that in the second coordination sphere; this result is in good agreement with the result for other complexes done by Sano *et al.*[12)]

As can be seen in Figs. 5, 6, and 7, the high-spin iron(II) and iron(III) species in [Fe(phen)$_2$Ox]·3H$_2$O, only the high-spin iron(II) species in [Fe(phen)$_2$Mal]·3H$_2$O, and two high-spin iron(II) species in [Fe(phen)$_2$F$_2$]·4H$_2$O are observed after irradiation. The absence of high-spin iron(III) species in [Fe(phen)$_2$Mal]·3H$_2$O after irradiation may be explained by the action of the carbon monoxide originating from the decomposition of the malonate ion, as has been reported in the cases of M[Mn(mal)$_2$] (M=NH$_4^+$, Na$^+$, and K$^+$) and K[Mn(mal)$_2$(H$_2$O)$_2$].[13)] A comparison of the infrared spectrum of the unirradiated [Fe(phen)$_2$Mal]·3H$_2$O with that of the irradiated one shows that the intensities of the C–O stretching appearing at 1610 and 1405 cm^{-1} were considerably decreased by the gamma-ray irradiation. This decrease suggests that carbonyl groups have been appreciably decomposed. The high-spin iron(II) species whose isomer shift is about 1.14 mm s^{-1} can be estimated to have a six-coordinated structure. The existence of the S=2 species in the irradiated [Fe(phen)$_2$Ox]·3H$_2$O and [Fe(phen)$_2$Mal]·3H$_2$O indicates that the ligand-field strength of the complex becomes weak. The configurational structure of a whole domain might retain the situation of total spin S=1, but in the spur formed in the path-way of ionizing radiation it might be changed to a state that is unable to maintain the situation of S=1 because of the local rearrangement of the configurational structure. The data obtained may support this assumption. Taking into account the value of the isomer shift (0.97 mm s^{-1}) of the newly produced species in [Fe(phen)$_2$F$_2$]·4H$_2$O upon irradiation, it is reasonable to regard the species as a tetrahedral compound formed by the elimination of F$^-$ from the coordination sphere. Such a tetrahedral species was not observed in the irradiated [Fe(phen)$_2$Cl$_2$]. This is because the atomic volume of Cl$^-$ is too large in comparison with that of F$^-$ to be removed from its coordination sphere.

No chemical changes were observed in all the samples listed in Table 5 except that the absorption intensities of [Fe(phen)$_3$](NO$_2$)$_2$·5H$_2$O and [Fe(phen)$_2$(NO$_2$)$_2$]·1/2H$_2$O decreased after irradiation.

It may be concluded that in the series of the iron complexes containing 1,10-phenanthroline as a ligand, low- and high-spin iron(II) compounds and high-spin iron(III) compounds, which have ligands with highly conjugated structures, are stable to gamma-ray irradiation. On the other hand, low-spin iron(III) compounds are sensitive to radiation.

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