2662 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 2662—2667 (1981) [Vol. 54, No. 9

The Correlation between the Bonding Properties of Ligands and the Irradiation Effects of Gamma-rays on Iron Compounds

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(Received August 5, 1980)

Various iron compounds have been irradiated with gamma-rays of cobalt-60. The foreign-charge states of the irradiated compounds were confirmed by means of Mössbauer spectroscopy. The results showed that high-spin iron(III) compounds with large conjugated molecules and low-spin iron(II) compounds are insensitive to γ-radiations. However, iron(III) compounds with carboxyl groups or reducing ligands and low-spin iron (III) compounds are sensitive to γ-radiations. Further, $FeCl_2 \cdot 4H_2O$ was found to be insensitive to radiation up to a total exposure dose of 10^9 R, in contrast to other ionic iron(II) compounds.

The gamma-ray sensitivity of solid coordination compounds has long been studied[1—6] and studies of the after-effect associated with the EC decay of ^{57}Co have increased in the past several years.[7—11] These after-effects have been attributed to radiolytic self-decomposition in the molecular environment of a decaying atom by low-energy electrons emitted during the Auger cascade, and to the subsequent stabilization of foreign-charge states by virtue of the redox properties of the radicals so produced. We have studied the effect of the electronic state and nature of the ligands on the sensitivity of iron compounds to gamma-ray irradiation by means of Mössbauer spectroscopy.

Experimental

The composition of the samples listed in Tables 1 and 2 was checked by elemental analyses for C, H, and N at the Elemental Analysis Center, Kyushu University. The phosphorus contents were colorimetrically determined with the formation of orthophosphate heteropoly blue using a molybdenum(V)–molybdenum(VI) reagent.[12] The results were in agreement with the calculated values. The metal complexes sealed in a glass tube *in vacuo* were irradiated with gamma-rays of 4000 Ci cobalt-60 in the Gamma-ray Irradiation Laboratory, Kyushu University. The irradiation was carried out at room temperature at a dose rate of 0.35—0.39×10^6 R h^{-1} or 1.17—1.19×10^6 R h^{-1}.

The Mössbauer spectra were measured immediately after the appropriate total exposure dose has been accumulated. Mössbauer measurements were carried out at 80 K with a spectrometer described elsewhere.[13] A cobalt-57 source diffused into a palladium foil was used. The isomer shift, δ_{Fe} was measured relative to the center of the spectrum of an iron foil enriched with ^{57}Fe at 296 K, which was also used as a standard material for the velocity calibration. The infrared spectra of the samples in the potassium bromide region(650—4000 cm^{-1}) were obtained using a Hitachi Grating Infrared Spectrophotometer, type 215.

Results and Discussion

Only the species stabilized during the irradiation of the investigated compounds were determined in the present study, since the Mössbauer measurements were carried out after an elongated irradiation. The Mössbauer parameters measured for the compounds before and after gamma-ray irradiation are listed in Tables 1 and 2. The Mössbauer data in Tables 1 and 2 were calculated using a least-squares method at the Computer Center, Kyushu University.

The compounds studied are classified into three groups in terms of the relation of the irradiation effects, such as the change in the oxidation state of iron with the chemical properties of the ligands, and the results of the Mössbauer spectra of the irradiated complexes are discussed in each case.

Group A. Group A consists of iron(III) compounds for which chemical changes were observed through the use of Mössbauer spectroscopy after irradiation.

A-1: This sub-group includes iron(III) compounds with only monodentate ligands. Compounds $FeCl_3 \cdot 2CH_3OH$, $[Fe(en)_3]Cl_3$ (en: ethylenediamine), $FeCl_3 \cdot$(1,4-dioxane), and $FeCl_3 \cdot$dma$\cdot 2H_2O$ (dma: *N,N*-dimethylacetamide) were sensitive to radiation. Some Mössbauer spectra of these compounds are shown in Figs. 1—3. New absorption lines due to bivalent iron were observed in the Mössbauer spectra of these compounds after irradiation. The ratio of the absorption area of the new lines to the total absorption area increased with the increase in the exposure dose, as is shown in Figs. 1 and 2. From this behavior

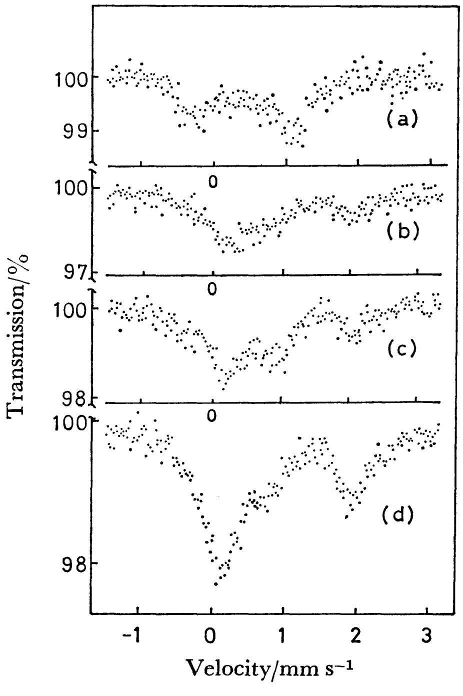

Fig. 1. Mössbauer spectra of $Fe(en)_3Cl_3$, (a) non-irradiated, (b) 4.4×10^8 R, (c) 11×10^8 R, and (d) 27×10^8 R irradiated.

Table 1. The Mössbauer parameters of the compounds before and after irradiation

	Compound	Exposure dose / 10^8 R	δ_{Fe}	ΔE	Γ_1[a)]	Γ_2[b)]	Remark
A-1	$FeCl_3 \cdot 2CH_3OH$	0	0.46	0.71	0.43	0.46	
		5.7	0.45	0.65	0.45	0.46	
			1.25	2.24	0.28	0.28	New[c)]
	$[Fe(en)_3]Cl_3$	0	0.21	1.29	0.69	0.90	
		11	0.19	1.36	0.25	0.51	
			1.07	1.85	0.62	0.35	New
	$FeCl_3 \cdot$(1,4-dioxane)	0	0.45	1.23	0.44	0.72	
		4.5	0.47	1.23	0.35	0.69	
			1.36	2.59	0.60	0.62	New
	$FeCl_3 \cdot dma \cdot 2H_2O$	0	0.34	0			
		1.6	0.35	0			
			1.13	2.43			
A-2	$FeCl_2gly(Hgly) \cdot \frac{7}{2}H_2O$	0	0.50	0.77	0.35	0.38	
		6.7	0.61	0.65	0.35	0.39	
			1.10	2.33	0.40	0.45	New
	$[Fe_3(HCO_2)_6][Fe(HCO_2)_6] \cdot 8H_2O$	0	0.53	0.86	0.45	0.45	
		9.0	0.51	0.93	0.45	0.46	
			1.32	2.55	0.5[d)]	0.6[d)]	New
A-3	$Fe(H_2PO_2)_3$	0	0.41	0.15	0.24	0.25	
		5.4	0.42	0.24	0.24	0.24	
			1.25	2.68	0.25	0.25	New
	$Fe_2(HPO_3)_3 \cdot 9H_2O$	0	0.53	0.48	0.28	0.28	
		8.3	0.54	0.42	0.35	0.35	
			1.37	2.27	0.48	0.48	New
A-4	$[Fe(bpy)_2(CN)_2]NO_3$	0	0.04	1.76	0.39	0.39	
		11	0.04	1.71	0.39	0.39	
			0.23	0.62	0.32	0.56	New

a) Full width at half-maximum of the lower energy peak. b) Full width at half-maximum of the higher energy peak. c) New peak due to irradiation. d) The errors are estimated to be ±0.1 mm s^{-1}. The errors of the other data are ±0.02 mm s^{-1} or less.

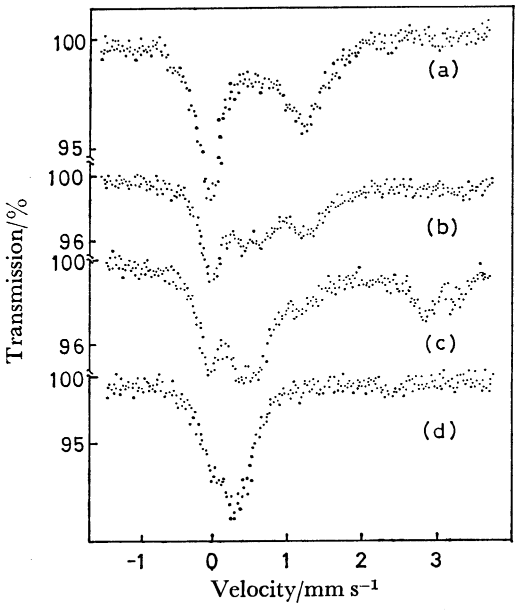

Fig. 2. Mössbauer spectra of $FeCl_3 \cdot$(1,4-dioxane), (a) non-irradiated, (b) 1.1×10^8 R, (c) 2.5×10^8 R, and (d) 4.5×10^8 R irradiated.

of the ratio, the iron(III) ion in these compounds is confirmed to be reduced to an iron(II) ion under irradiation.

Figure 1 shows the Mössbauer spectra for $[Fe(en)_3]Cl_3$ at successive stages of irradiation. Compound $[Fe(en)_3]Cl_3$ is in a low-spin state. The Mössbauer parameters of the new lines produced by irradiation are as follows: The quadrupole splitting, $\Delta E = 1.85$ mm s^{-1}; the isomer shift, $\delta_{Fe} = 1.07$ mm s^{-1}. These values range among those for high-spin iron(II) compounds. The Mössbauer parameters for $[Fe(en)_3]Cl_2$ have not yet been reported because the compound is very unstable in air. It is very probable, however, that the orbital ground state of $[Fe(en)_3]Cl_2$ is in a high-spin state as a result of the strength of the ligand field of ethylenediamine.[14)] The isomer shift of 1.07 mm s^{-1} at 80 K is smaller than that for high-spin hexacoordinated iron(II) compounds. However, the radiolysis of ethylenediamine ligands might have resulted in a smaller coordination number about the central iron atom, thus causing a small value of the isomer shift because of the change in bonding from d^2sp^3 hybridized orbitals to sp^3.

In the IR spectrum of the irradiated $FeCl_3 \cdot 2CH_3OH$, new lines appeared at 2850 and 2900 cm^{-1}; they are assigned to the vibration of the C–H of a formyl group. A characteristic vibration band for the formyl group appears at about 1700 cm^{-1},[15)] but this band

TABLE 2. THE MÖSSBAUER PARAMETERS OF THE COMPOUNDS BEFORE AND AFTER IRRADIATION

	Compound	Exposure dose / 10^8 R	δ_{Fe}	ΔE	Γ_1	Γ_2
B-1	$FeCl_3(pyrazole)_3$	0	0.50	0	1.09	
		10	0.45	0	1.11	
	$Fe(koj)_3$[a]	0	0.55	0.96	0.35	0.49
		10	0.48	1.01	0.36	0.48
	$[Fe(bpy)_2Cl_2][FeCl_4]$	0	0.40 0.44	0 0.33	0.45 0.47	 0.47
		10	0.29 0.41	0 0.47	0.47 0.44	 0.44
	$[Fe(pyridine)_5ClO_4](ClO_4)_2$	0	0.39	0.66	0.65	0.65
		10	0.46	0.76	0.67	0.59
B-2	$[Co(pn)_3][FeCl_6]$	0	0.46	0.26	0.29	0.29
		16	0.47	0.17	0.29	0.29
	$[Co(NH_3)_6][FeCl_6]$	0	0.47	0	0.40	
		12	0.55	0	0.40	
	$Fe_3(OCH_3)_9$	0	0.44	0.37		
		17	0.46	0.42	0.69	0.51
	$FePO_4 \cdot 2H_2O$	0	0.67	0.18	0.25	0.25
		10	0.66	0.18	0.25	0.25
C-1	$Fe(phen)_2Cl_2$	0	1.08	3.26		
		10	1.12	3.30		
	$Fe(H_2PO_2)_2$	0	1.29	2.68	0.26	0.26
		10	1.32	2.73	0.24	0.24
	$FeCl_2 \cdot 4H_2O$	0	1.36	3.12		
		10	1.35	3.12	0.29	0.30
C-2	$[Fe(bpy)_3]Cl_2 \cdot 4H_2O$	0	0.40	0.37	0.31	0.27
		10	0.39	0.35	0.44	0.34
	$Fe(bpy)_2(CN)_2 \cdot 4H_2O$	0	0.19	0.62	0.34	0.34
		10	0.26	0.65	0.36	0.38
	$[Fe(phen)_3](NO_2)_2 \cdot 5H_2O$	0	0.35	0.27	0.26	0.26
		10	0.39	0.27	0.33	0.32
	$Fe(phen)_2(NO_2)_2 \cdot \frac{1}{2}H_2O$	0	0.33	0.42	0.27	0.31
		10	0.34	0.42	0.27	0.32

a) koj: kojate ion.

is obscured because of overlapping with the very strong band at 1600 cm^{-1}. The reduction of iron(III) chloride in a methanol solution has been studied extensively.[16] The production of H_2, CH_2O, CH_4, and glycol has been reported. The following steps are inferred to be involved in the reaction induced by the gamma-ray irradiation of $FeCl_3 \cdot 2CH_3OH$ on the assumption that the radiolysis of $FeCl_3 \cdot 2CH_3OH$ undergoes a series of reactions similar to those of iron(III) chloride in a methanol solution:[17]

$$CH_3OH \longrightarrow \cdot CH_2OH + \cdot H$$

$$Fe^{3+} + \cdot CH_2OH \longrightarrow Fe^{2+} + HCHO + H^+$$

$$Fe^{3+} + \cdot H \longrightarrow Fe^{2+} + H^+$$

$$Fe^{3+} + Cl^- \longrightarrow Fe^{2+} + Cl.$$

The $Fe_3(OCH_3)_9$ compound was insensitive to radiation, as will be described later. The $\cdot CH_2OH$ radical may be reactive in redox reactions, while CH_3O^- may not.

Figure 2 shows the Mössbauer spectra for irradiated $FeCl_3 \cdot (1,4\text{-dioxane})$ at successive stages of irradiation. Iron(II) ions initially reduced by gamma-ray irradiation are oxidized to iron(III) ions upon further irradiation. The total exposure dose of 4.5×10^8 R causes serious damage to this compound, as may be seen in Fig. 2(d). The main decomposition products of dioxane have been reported to be HCHO(G=9.7), $HCOO\text{–}CH_2\text{–}CH_2OH$($G$=8.5), and H_2(G=1.4).[18]

The compound $FeCl_3 \cdot dma \cdot 2H_2O$ was also sensitive to radiation. That is, iron(II) absorption lines were observed in the Mössbauer spectrum of this compound after irradiation. The new bands found in the IR spectrum can be assigned to the formyl, which is known to have absorption in the region from 2800 to 2900 cm^{-1}.

A-2: This sub-group is composed of iron(III) compounds with a carboxyl group. Glycine(Hgly) is comprised of carboxyl and amino groups. The carboxyl group is known to be very sensitive to radiation and to produce reductive radicals, as has been reported by many workers.[19,20] The G values ($Fe^{3+} \rightarrow Fe^{2+}$) for $FeCl_2 \cdot gly(Hgly) \cdot 7/2H_2O$ and $[Fe_3(HCO_2)_6]$ $[Fe(HCO_2)_6] \cdot 8H_2O$ were estimated to be about 2.5±

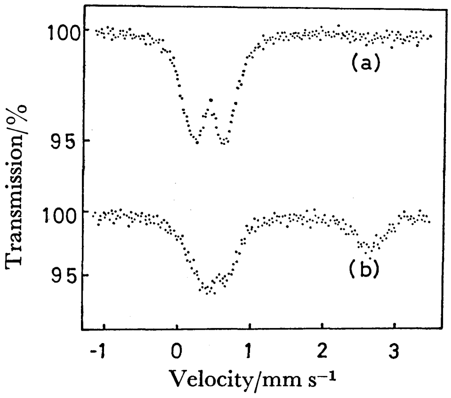

Fig. 3. Mössbauer spectra of (a) non-irradiated and (b) 8.3×10^8 R irradiated $Fe_2(HPO_3)_3\cdot9H_2O$.

0.5 (at a total exposure dose of 6.7×10^8 R) and 3.2 ± 0.5 (at a total exposure dose of 9.0×10^8 R) respectively from analyses of the Mössbauer spectra using equation:

$$G=\frac{\dfrac{A_I(\text{the absorption area of a new peak})}{A(\text{the total absorption area})}}{\text{the absorption energy(eV)}}\times 100$$

and assuming that the recoilless fractions of the original peaks and the new peaks are equal, and that an exposure dose of 1 R gives an absorbed dose of 1 rad for these compounds. The initial G values, however, will be larger than these values.

A-3: This sub-group is composed of iron(III) compounds with reducing ligands. The $H_2PO_2^-$ and HPO_3^{2-} ions are considered to be reducing ions. The iron(III) ions in $Fe(H_2PO_2)_3$ and $Fe_2(HPO_3)_3\cdot9H_2O$ were reduced to iron(II) ions under irradiation. The G value of the decomposition for $Fe(H_2PO_2)_3$ is reported to be 3.4 ± 0.4[21] and the main decomposition products after it had been dissolved in water were confirmed chemically to be phosphate and phosphonate ions.[22,23] That is, the P(I) ligand is oxidized to P(III) and P(V) under irradiation. Figure 3 shows the Mössbauer spectra for $Fe_2(HPO_3)_3\cdot9H_2O$ before and after irradiation. The oxidation state of phosphorus of this compound is trivalent, and may be oxidized to P(V) upon irradiation.

A-4: This sub-group is composed of iron(III) compounds with a low-spin state. The Mössbauer parameters of the new lines for irradiated $[Fe(bpy)_2(CN)_2]NO_3$(bpy: 2,2′-bipyridyl) were $\Delta E=0.62$ mm s⁻¹, $\delta_{Fe}=0.23$ mm s⁻¹. These values are similar to those of nonirradiated $Fe(bpy)_2(CN)_2$ ($\Delta E=0.62$ mm s⁻¹, $\delta_{Fe}=0.19$ mm s⁻¹). This similarity of the Mössbauer parameters suggests that the iron(II) ion produced under irradiation has the same coordination structure as the nonirradiated $Fe(bpy)_2(CN)_2$. The iron(III) ion of $[Fe(phen)_3](ClO_4)_3\cdot2H_2O$ has been reported to be reduced to the Fe(II) ion upon irradiation.[4] The iron(III) compounds in a low-spin state may be supposed to be reduced to iron(II) easily upon irradiation, although they contain large conjugated ligands.

Group B. Group B consists of iron(III) compounds in which no change of valence was observed in the Mössbauer spectra. The Mössbauer parameters of these compounds are shown in Table 2. A total exposure dose of 1×10^9 R or more was delivered to the compounds of this group.

B-1: This sub-group is made up of iron(III) compounds with large conjugated ligands. In this group, no reduced iron(II) species were observed in the Mössbauer spectra after irradiation. Iron(III) kojate and $FeCl_3\cdot$(pyrazole)$_3$ show broad Mössbauer spectra attributable to a relaxation effect. There was no change in the width at the half-maximum in the spectra between before and after irradiation. Although a part of the ligands are initially excited upon irradiation, the excitation energy is considered to be distributed in a short time through the conjugated bonds and delocalized over all of the molecules. Therefore, the fragmentation and the excitation of the molecules due to irradiation may be minimized. Compounds $[Fe(bpy)_2Cl_2][FeCl_4]$ and $[Fe(pyridine)_5ClO_4](ClO_4)_2$ were also insensitive to radiation.

B-2: This sub-group is made up of iron(III) compounds without large conjugated ligands. No influence of radiation was observed in $[Co(pn)_3][FeCl_4]$ (pn: 1,2-propanediamine) and $[Co(NH_3)_6][FeCl_6]$, although the radiolysis of 1,2-propanediamine and ammonia would be expected because iron(II) species are observed in the spectra of irradiated $[Fe(en)_3]Cl_3$. This fact shows that the iron ion is well shielded in $[Co(pn)_3][FeCl_4]$ and $[Co(NH_3)_6][FeCl_6]$ by the large volume of chloride ions from the electrons and the radicals produced upon irradiation.

Each iron atom in $FePO_4\cdot2H_2O$ is surrounded by four oxygen atoms of the PO_4^{3-} ions and two oxygen atoms of the water molecules.[24] The oxygen atoms of the PO_4^{3-} ions, however, coordinate tetrahedrally to the iron atom as the nearest atoms, and the two oxygen atoms of water molecules coordinate to the iron atom as the next nearest atoms. It is concluded that the radicals resulting from the radiolysis of water molecules were not able to react with the central iron(III) atom during the life-time of the radicals because the distance between the iron atom and water molecules is large, or because the iron atom is shielded by the four oxygen atoms of PO_4^{3-} ions from the electrons and the radicals as has been described above. The influence of the radiolysis of water molecules on the redox of the iron atom was not observed for the compounds studied in this paper. One of the reasons for this is that the $G(-H_2O)$ value for the decomposition of the water is as small as 0.1. The $G(-H_2O)$ value is less than 0.01 for the hydrates, whereas for ice it is known to be greater than 0.1.[25]

Compound $Fe_3(OCH_3)_9$ was also insensitive to radiation, although the bond-dissociation energy of methanol is 389 kJ mol⁻¹ for $HOCH_2$–H, 383 kJ mol⁻¹ for H_3C–OH, and 418 kJ mol⁻¹ for CH_3O–H,[26] and the bond-dissociation energies of $HOCH_2$–H and H_3C–OH are lower than that of CH_3O–H. The following reaction of the hydrated electron is known in the pulse radiolysis of a water–methanol solution:[17]

$$e_{aq}^- + CH_3OH \longrightarrow CH_3O^- + H$$

$$e_{aq}^- + CH_3OH \longrightarrow CH_3 + OH^-.$$

In a solid phase, the bare electron produced by ir-

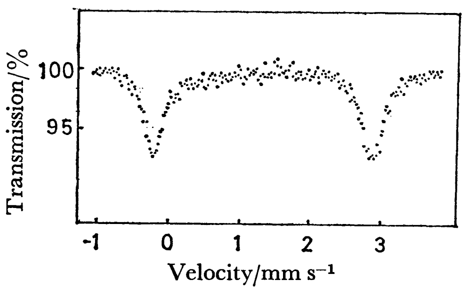

Fig. 4. Mössbauer spectrum of 10×10^8 R irradiated $FeCl_2\cdot4H_2O$.

radiation may take the place of the hydrated electron. Thus, CH_3O^- would not react with electrons and the $G(H_2)$ from $Fe_3(OCH_3)_9$ would be smaller than that from $FeCl_3\cdot2CH_3OH$.

Group C. Generally, high-spin iron(II) compounds, such as $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$ and $FeSO_4\cdot7H_2O$, are easily oxidized to basic iron(III) species upon irradiation.[27] Although the iron(II) ions of both compounds are surrounded by six water molecules, the reducing radicals produced from the decomposition of the water may react with other species, such as NH_4^+ and SO_4^{2-}, by preference, for the Fe(III) ion, the sulfite ion, and hydrogen have been reported to exist as products of decomposition.[28]

Group C consists of iron(II) compounds in which no chemical change was observed through the Mössbauer spectra. The compounds of this group were subjected to a total exposure dose of 1.0×10^9 R or more.

C-1: This sub-group contains high-spin iron(II) compounds in which no change of valence was observed. That is, $Fe(H_2PO_2)_2$ and $FeCl_2\cdot4H_2O$ were insensitive to radiation up to an exposure dose of 1.0×10^9 R.

The $H_2PO_2^-$ anion is a strong reducing ion. The decomposed fractions of $H_2PO_2^-$ in 400 Mrad delivered $Fe(H_2PO_2)_2$ and $Fe(H_2PO_2)_3$ were 5 and 10% respectively.[21] The compounds with a lower valent iron(II) ion and a strong reducing anion, iron (II) oxalate, are also radioresistant.[1] The remarkably high stability upon the irradiation of these compounds must involve the process of the recombination of radicals and electrons due to the absence of a redox reaction between radicals and central metal ions.

Figure 4 shows the Mössbauer spectrum of irradiated $FeCl_2\cdot4H_2O$. This compound contains four water molecules which are arranged around an iron(II) ion.[29] It is easy for the radicals produced from the radiolysis of water molecules to react with an iron(II) ion because water molecules are coordinated directly with the iron(II) ion. Nevertheless, the iron ion of $FeCl_2\cdot4H_2O$ was not oxidized to an iron(III) ion. This suggests that the radicals formed on the radiolysis of H_2O will be inclined to participate in the recombination reaction, as the chloride ion is not easily oxidized or reduced. Kopcewicz *et al.*[30] reported that they observed the Fe_3O_4, $Fe_{1-x}O$, and $FeCl_2\cdot2H_2O$ species, in proton-irradiated $FeCl_2\cdot4H_2O$. The effects observed were interpreted in terms of the "thermal spike" model. Friedt *et al.*[31] reported the emission spectra of $^{57}CoCl_2\cdot X(X=2H_2O$ and $6H_2O)$ to show the existence of two kinds of Fe(III) species and two kinds of Fe(II) species, due to the self-radiolysis of the ligand environment by the low-energy electrons and X-rays emitted during the Auger cascade. As our experimental method has the limitation that only stabilized changes after irradiation can be observed the metastable species with a short lifetime can not be observed in the Mössbauer spectra. Emission experiments, on the other hand, might sometimes show the metastable state. Compound $Fe(bpy)_2Cl_2$, which has a high degree of conjugation, showed no chemical change due to irradiation.

C-2: This sub-group is composed of the low-spin iron(II) compounds. Compounds $[Fe(bpy)_3]Cl_2\cdot4H_2O$, $[Fe(bpy)_2(CN)_2]\cdot4H_2O$, $[Fe(phen)_3](NO_2)_2\cdot5H_2O$-(phen: 1,10-phenanthroline), and $[Fe(phen)_2(NO_2)_2]\cdot1/2H_2O$ were insensitive to radiation, and the oxidation state of iron(III) was not observed in the Mössbauer spectra up to an exposure dose of 1.0×10^9 R.

The electron configurations of high-spin iron(II) and iron(III) ions in octahedral complexes are $t^4_{2g}e^2_g$ and $t^3_{2g}e^2_g$ respectively. The reduction of the iron(III) ion to the iron(II) ion results in the transfer of an electron from ligands to a t_{2g} orbital of the Fe (III) ion, the rate of which is faster than that to an e_g orbital in an octahedral complex.[32] The situation is the same for iron ions in a low-spin state in an octahedral complex, for the electronic configurations of the low-spin iron(II) and iron(III) ions are t^6_{2g} and t^5_{2g} respectively. However, some of the compounds were highly radioresistant. The high-spin iron(III) compounds with large conjugated ligands and low-spin iron(II) compounds exhibited especially strong radioresistant properties. The fact that the orbital ground states of high-spin iron(III) and low-spin iron (II) ions have more stability than high-spin iron(II) and low-spin iron(III) ions respectively would affect the reaction of electrons and radicals formed under the action of radiation, thus leading to the observed stability of the compounds of both categories upon irradiation.

The width of the Mössbauer spectra of the compounds which were insensitive to radiation became broad, and the spectra showed a little distortion. This means that considerable damage in the coordination structure has taken place under irradiation, although no changes in the valence of the iron ion were detected in the Mössbauer spectra.

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