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MÖSSBAUER STUDY OF IRRADIATED IRON CHELATES AND CHEMICAL CONSEQUENCES OF ^{57}Co ELECTRON CAPTURE IN COMPLEX LIGAND COMPOUNDS

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INTRODUCTION

Chemical after-effects of ^{57}Co electron capture (EC) have been observed by Mössbauer emission spectroscopy in a variety of matrices (1). There is generally good agreement between independent experimental data, but detailed understanding of the stabilization mechanism of the defect charge states is only developing.

EC decay of ^{57}Co is followed by an Auger ionization cascade which leads to multiply charged $^{57}Fe^{n+}$ ions ($n \leq 7$ in $^{57}Co^{2+}$ (2)) on a time scale of 10^{-15}s (3). The Mössbauer emission spectroscopy allows the observation of these charge states provided their life-time is higher than or comparable to 10^{-7}s, i.e. the mean life-time of the first excited state of the ^{57}Fe nucleus. The neutralization of the highly charged ions has been shown from time-delayed coincidence

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measurements to proceed faster than this characteristic time-scale of 10^{-7}s (4). Thus, only longer lived species are observed in Mössbauer emission spectroscopy.

Mass spectrometric experiments have shown that molecules in the gaseous phase are fragmented by a coulombic repulsion process after an inner shell ionization of a central atom. The high positive charge built up upon this atom is partially neutralized by electron transfer from the rest of the molecule, thus inducing repulsive forces between the positively charged ligands. The validity of this mechanism has been amply demonstrated in the gaseous phase but has not yet been proved in a condensed medium. Nevertheless, several authors have recently suggested that a similar mechanism could prevail after ^{57}Co electron capture in molecular complexes (5).

During the ionization cascade, Auger electrons and x rays are emitted. The energies of the Auger electrons emitted from the L or more extended shells are low (of the order of magnitude of 50 eV) so that they have a very short range. They dissipate their energy very locally, providing an autoradiolysis of the ligands around the site of the decayed nucleus. This process has been invoked to account for the chemical states of the iron species inferred from the Mössbauer emission spectra (6). As suggested by Wertheim et al. (7), an internal autoradiolysis should be well simulated by the irradiation with an external radiation source, i.e. electrons. Preliminary results of the Mössbauer analysis of the irradiated Fe(III) acetylacetonate have already been reported (8).

EXPERIMENTAL

Chemicals:

Fe(III) acetylacetonate $\left[Fe^{III}(Acac)_3\right]$ was a commercial reagent grade product from Fluka AG. Fe(II) tris-dipyridyl perchlorate $\left[\left[Fe^{II}(dipy)_3\right](ClO_4)_2\right]$

was kindly provided by Dr. P. Krumholz (9) as a highly purified material in well crystallized form. Fe(III) tris-dipyridyl perchlorate $\left[\left[Fe^{III}(dipy)_3\right] (ClO_4)_3\right]$ was prepared according to a recipe communicated by Dr. Krumholz: bipyridine reacted in stoichiometric amounts with ferric chloride in alcoholic solution, and the complex was precipitated after addition of $NaClO_4$. All operations were conducted at ice temperature. Fe(III) citrate was obtained from neutralization of citric acid by freshly precipitated ferric hydroxide at controlled pH (10). Fe(II) citrate was prepared by reaction of iron powder with citric acid, and subsequent precipitation by addition of alcohol in a reducing atmosphere (11). Sodium ethylenediamine tetraecetate Fe(III) [[Fe(III) EDTA]] has been prepared according to the method given by Spijkerman et al. (12).

PROCEDURE

About 100 mg of the complexes were mounted in a liquid nitrogen cryostat. The 2 MeV electron beam (from a travelling wave pulsed linear accelerator) crossed the windows of the cryostat.

The average beam current was 5μA and the temperature of the sample during the irradiation was kept at 160°C. Generally, the irradiation time required for an appreciable change in the Mössbauer spectra was 30 minutes (corresponding to a total dose of about 1800 Mrad) (13).

The Mössbauer spectra were measured with a conventional constant acceleration spectrometer, with a ^{57}Co: Pd source of 15 mCi.

The annealing experiments were conducted by warming the samples up to room temperature in vacuum inside the cryostat used for the irradiation and the measurement.

The ESR spectra of the samples irradiated at liquid nitrogen temperature in evacuated and sealed glass tubes were measured with a Varian spectrometer.

EXPERIMENTAL RESULTS

Figures 1 to 4 show the Mössbauer absorption spectra of irradiated ferric citrate, Fe(III) EDTA, tris-dipyridil Fe(III) perchlorate and Fe(III) acetylacetonate and the emission spectra of the corresponding cobalt complexes labelled by ^{57}Co (5). In all cases, a clear similarity appears between the line positions in the emission and absorption spectra, indicating that the species stabilized after ^{57}Co EC are similar to those formed by radiolysis in an external irradiation source. Test experiments without irradiation have shown that the appearance of the new lines was not due to a spontaneous decomposition of the complexes. Quite generally, an increase of the proportion of the new species with the irradiation time has been observed.

The attribution of the new lines appearing in the absorption spectra after radiolysis cannot be achieved unequivocally for Fe(III) acetylacetonate since the corresponding Fe(II) complex is unknown. These lines are however characteristic of high-spin ferrous ions. The identification of the new lines appearing in the spectra of the other irradiated complexes is not difficult. Figure 5 shows the spectra of unirradiated $\left[Fe^{II}(dipy)_3\right](ClO_4)_2$ and $\left[Fe^{III}(dipy)_3\right](ClO_4)_3$ and the spectrum of the irradiated ferric complex. The latter spectrum clearly results from a superposition of the lines of the ferrous and ferric complexes. The radiolytic decomposition of $\left[Fe^{III}(dipy)_3\right](ClO_4)_3$ leads to a partial reduction into the Fe(II) complex. Similarly, after ^{57}Co EC in $\left[Co^{III}(dipy)_3\right](ClO_4)_3$, ^{57}Fe stabilizes in the ferric and ferrous forms. In the limit of the sensibili-

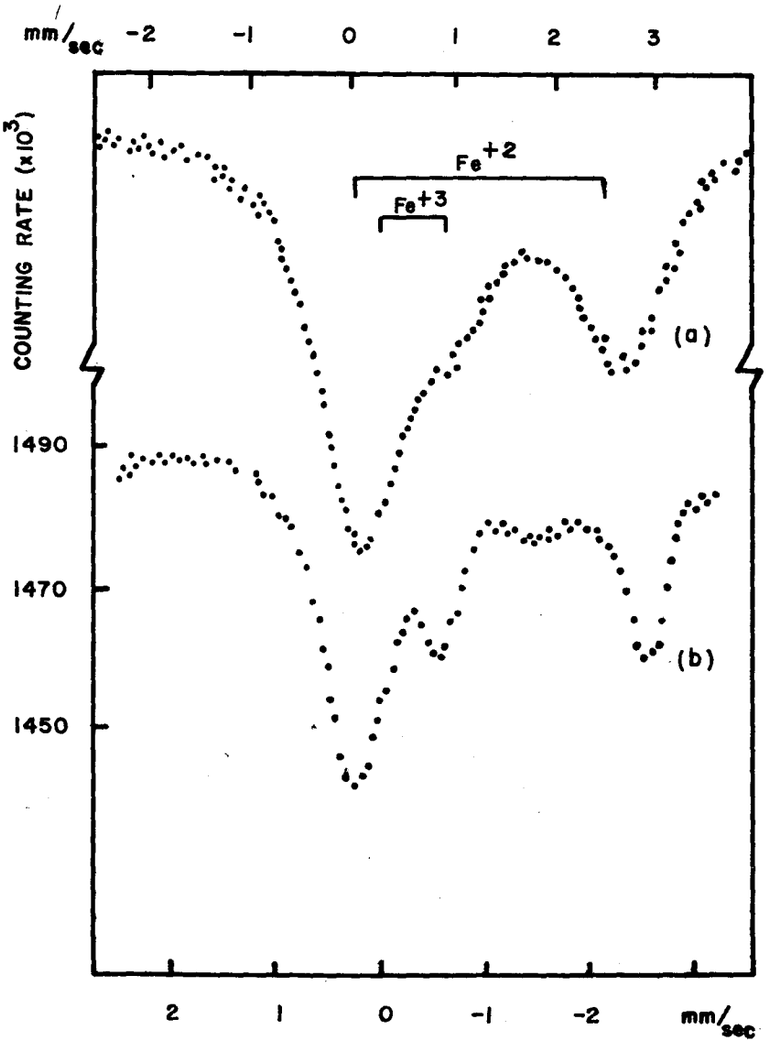

Figure 1 - Mössbauer emission spectrum of ^{57}Co: Co^{III} citrate at 77°K (a) (from ref. 5) and absorption spectrum of electron irradiated Fe^{III} citrate at 80°K (irradiation at 113°K) (b).

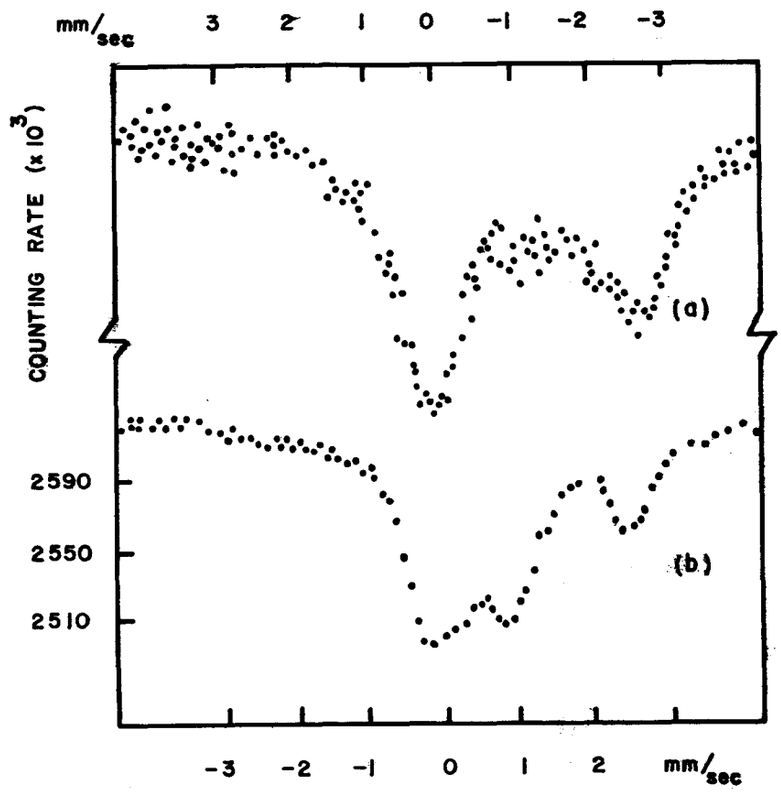

Figure 2 - Mössbauer emission spectrum of ^{57}Co: Co^{III} EDTA at 77°K (a) (from ref. 5) and absorption spectrum of electron irradiated Fe^{III} EDTA at 80°K (b).

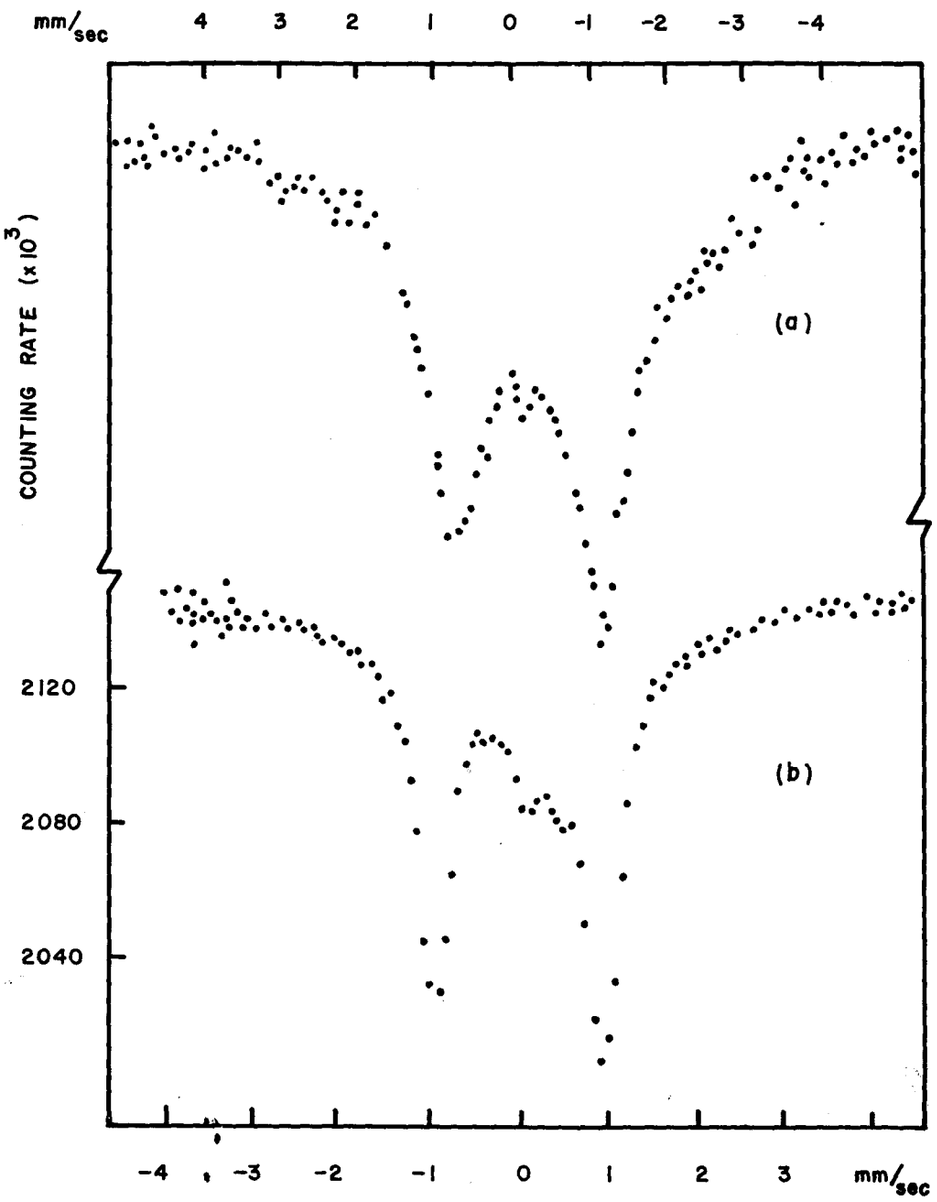

Figure 3 - Mössbauer emission spectrum of ^{57}Co: $|Co^{III}(dipy)_3|(ClO_4)_3$ at 77°K (a) (from ref. 5) and absorption spectrum of electron irradiated $|Fe^{III}(dipy)_3|(ClO_4)_3$ at 80°K (b).

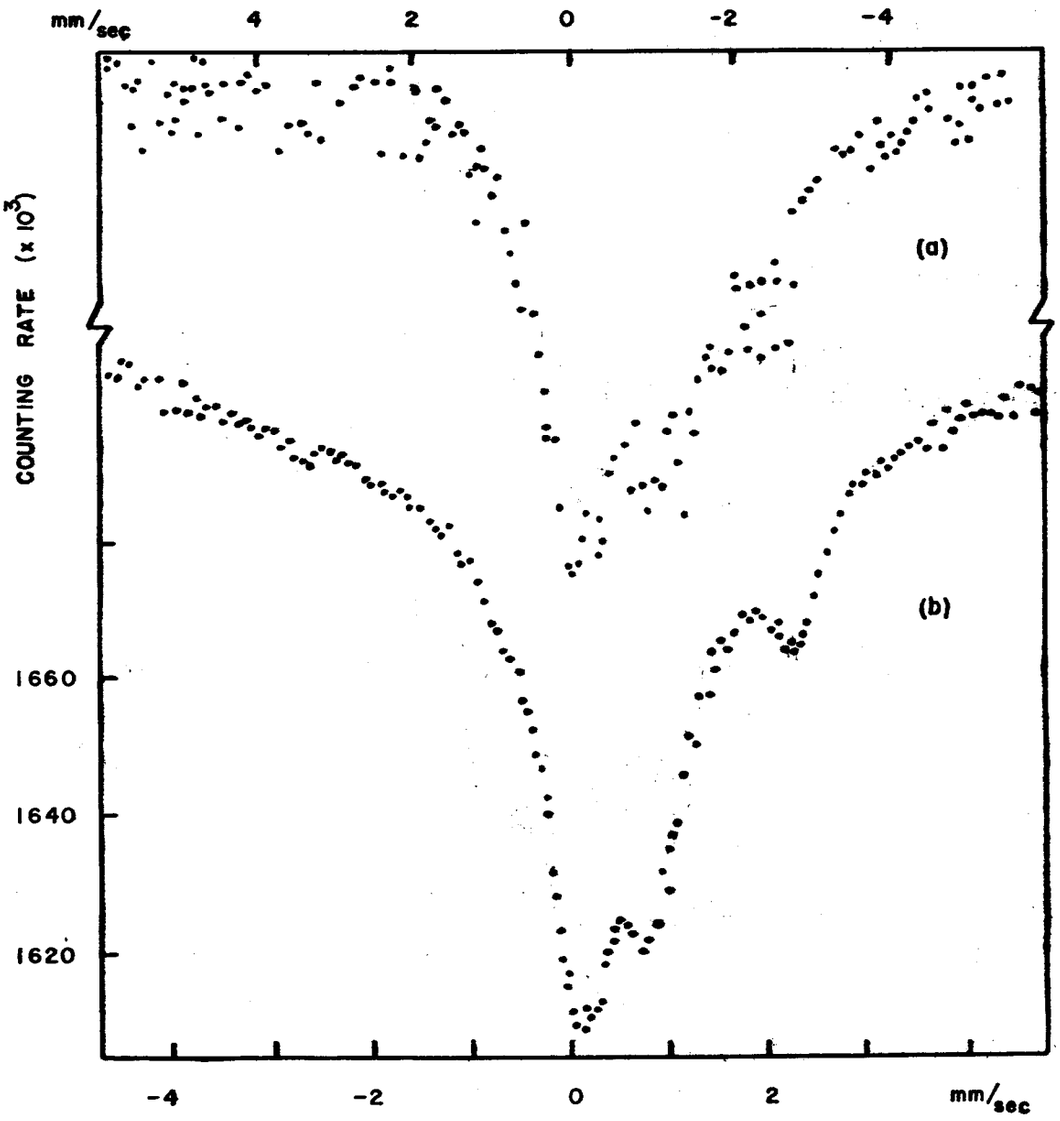

Figure 4 - Mössbauer emission spectrum of ^{57}Co: Co (Acac)$_3$ at 77°K (a) (from ref. 5) and absorption spectrum of electron irradiated $^{Fe^{III}}$(Acac)$_3$ at 80°K (b).

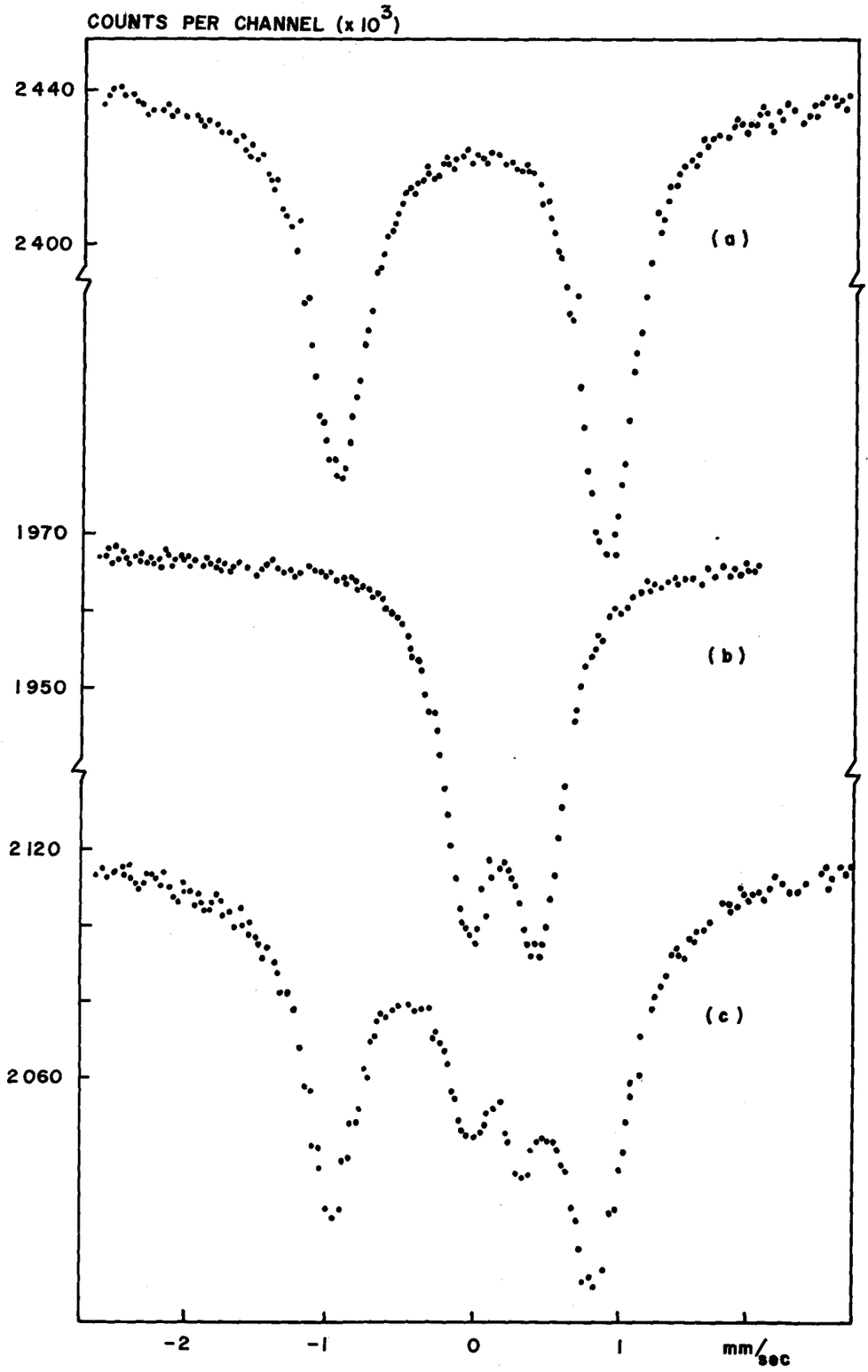

Figure 5 - Mössbauer absorption spectra at 80°K of
(a) $|Fe^{III}(dipy)_3|(ClO_4)_3$
(b) $|Fe^{II}(dipy)_3|(ClO_4)_2$
(c) irradiated $|Fe^{III}(dipy)_3|(ClO_4)_3$

ty of the method, no other molecular complexes could be detected after irradiation.

The Mössbauer parameters deduced from the emission and the absorption spectra for the various compounds are reported in table I. As for $\left[Fe^{III}(dipy)_3\right](ClO_4)_3$ a radiolytic reduction of Fe(III) citrate, $Fe^{III}(Acac)_3$ and Fe(III) EDTA is observed. The radiolytic and photolytic reduction of Fe(III) citrate have been observed recently by Buchanan (14) and Saito et al (15).

Annealing experiments have been carried out at room temperature. In $Fe^{III}(Acac)_3$ the annealing becomes complete after 12 hours storage: the Mössbauer spectrum of the unirradiated complex reappers (figure 6). The annealing rate is much slower for ferric citrate (figure 7) and for Fe(III) EDTA (figure 8). On the other hand, for $\left[Fe^{III}(dipy)_3\right](ClO_4)_3$ an annealing experiment at 270°K induces a further reduction into the Fe(II) complex (figure 9); it has been checked independently that the original product does not decompose spontaneously in similar conditions of storage. In order to see if the reduction of the iron complexes involves a free-radical mechanism induced by the radiolysis of the organic ligands, the ESR spectra of the irradiated materials were investigated. With the exception of $\left[Fe^{III}(dipy)_3\right](ClO_4)_3$, no free radicals were detected. On the other hand, an irradiation with a much lower dose (2 MeV electrons, 5µA during 30 s at 80°K) of the sodium salts of the organic ligands considered in this work led to the observation of free radicals in all cases. These results agree with the observations reported by other authors in ESR studies of several irradiated chelates, i.e. no ESR spectra could be detected in chelates containing a transition metal ion with a high oxidation potential (such as the iron complexes) (18).

	Acetylacetonate		Citrate		EDTA		Tris-dipyridyl perchlorate	
	IS	QS	IS	QS	IS	QS	IS	QS
Fe(III) 77°K	0.38±0.05	0.51±0.05	0.32±0.03	0.54±0.05	0.35±0.03		-0.06±0.05	1.83±0.05
Fe(II) 77°K			1.20±0.05	3.38±0.05	1.17*	2.80*	0.22±0.05	0.42±0.05
295°K			1.09±0.05	2.78±0.05			0.145±0.05	0.38±0.03
New peaks after irradiation assigned to Fe(II)								
77°K	1.04±0.05	2.22±0.05	1.13±0.05	2.79±0.05	1.06±0.05	2.70±0.06	0.22±0.05	0.38±0.05
295°K							0.19±0.05	0.37±0.05

* From L. M. Epstein, J. Chem. Phys. 36, 2731 (1962).

TABLE 1: Mössbauer parameters of Fe(III) and Fe(II) complexes (for comparison, see ref. 12, 16 and 17) and of the peaks appearing after the electron irradiation of the Fe(III) complexes. IS values refer to ^{57}Co: Pd. All values are given in mm/s.

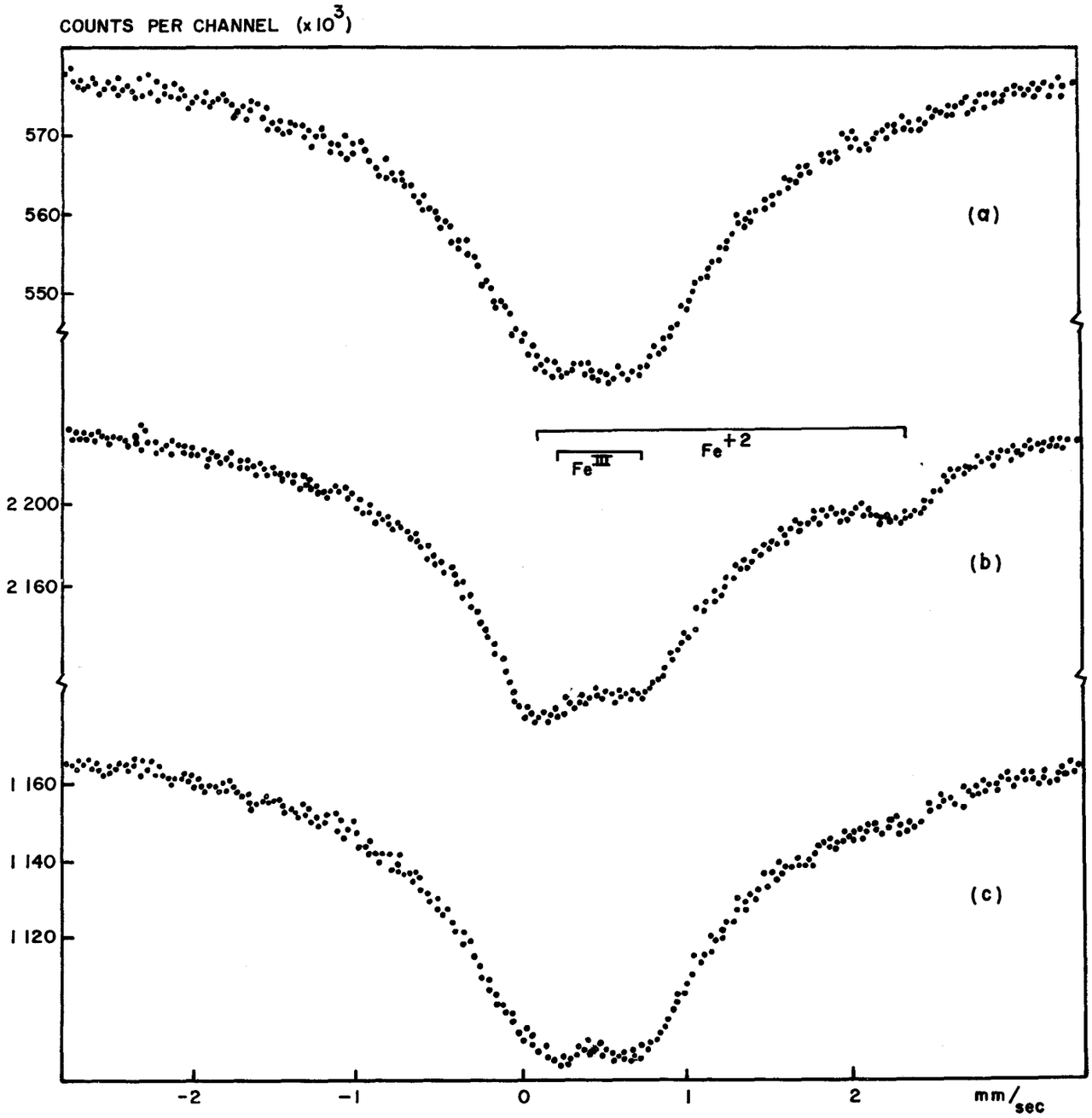

Figure 6 - Mössbauer absorption spectra at 80°K of Fe^{III} $(Acac)_3$

(a) unirradiated

(b) irradiated

(c) irradiated and annealed at room temperature during 12 hours.

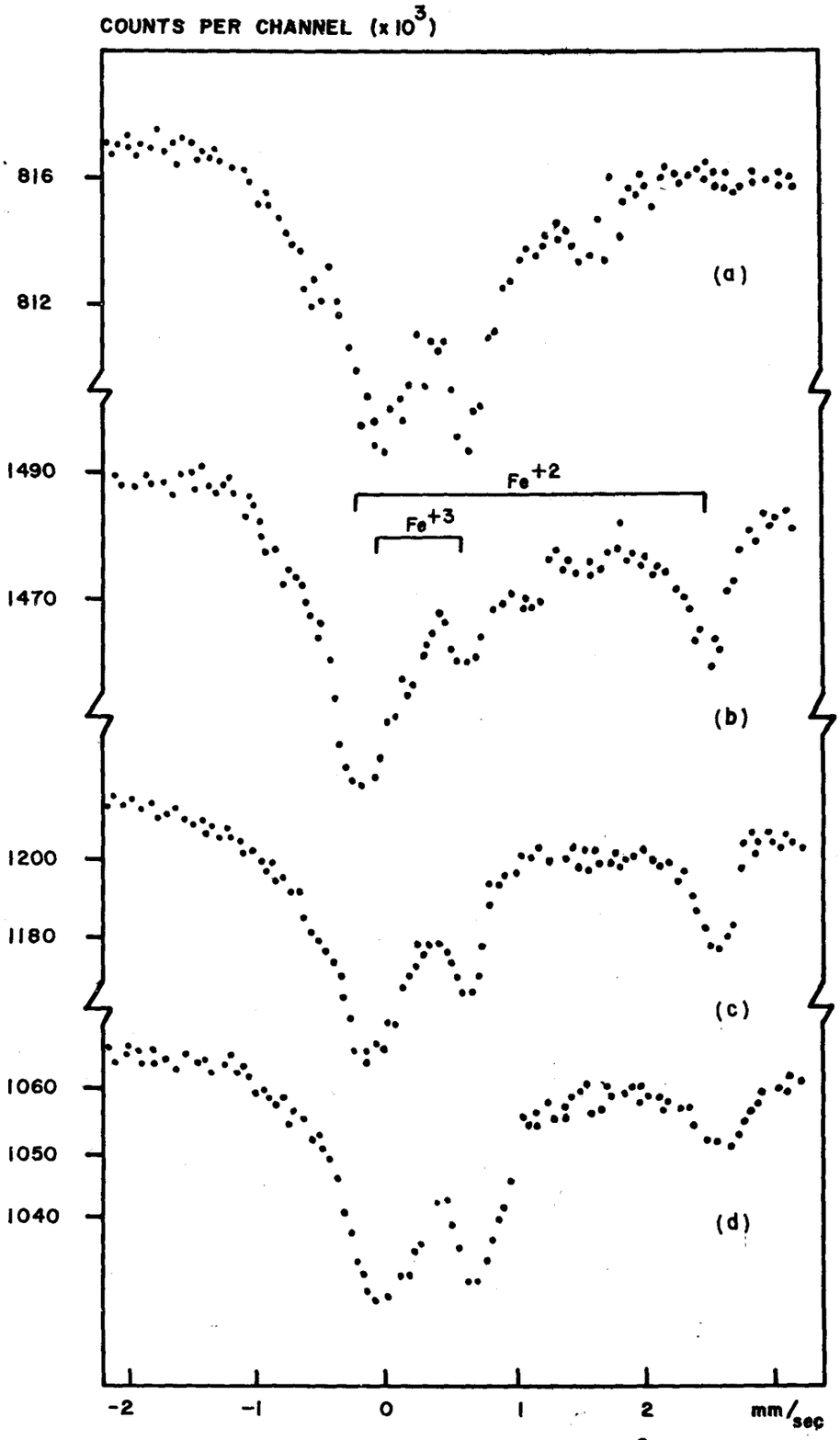

Figure 7 - Mössbauer absorption spectra at 80°K of Fe(III) citrate

(a) unirradiated

(b) irradiated

(c) irradiated and annealed at room temperature during 2 days

(d) after annealing at room temperature during 10 days.

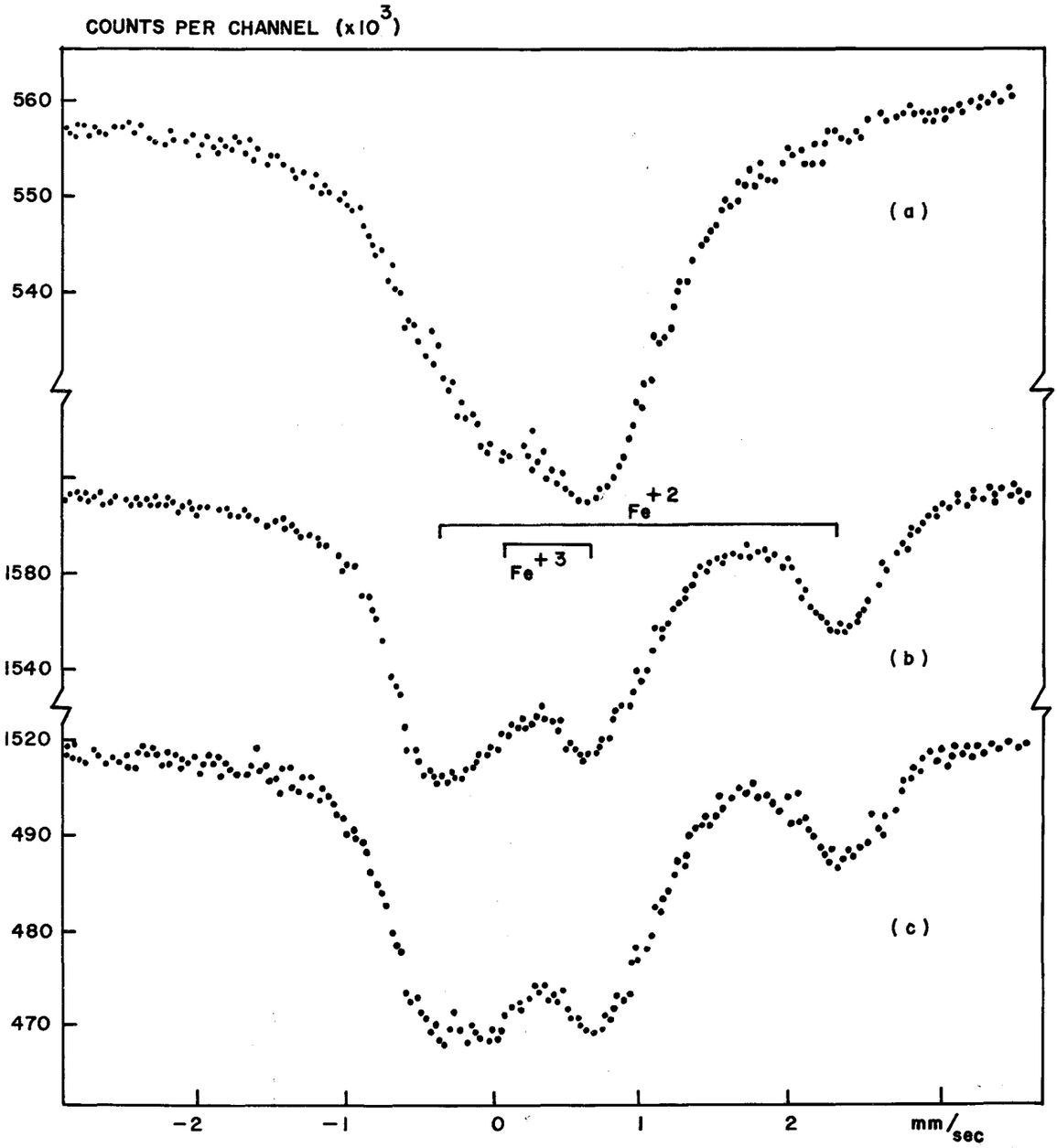

Figure 8 - Mössbauer absorption spectra at 80°K of Fe^{III} EDTA

(a) unirradiated

(b) irradiated

(c) irradiated and annealed at 330°K during 12 hours.

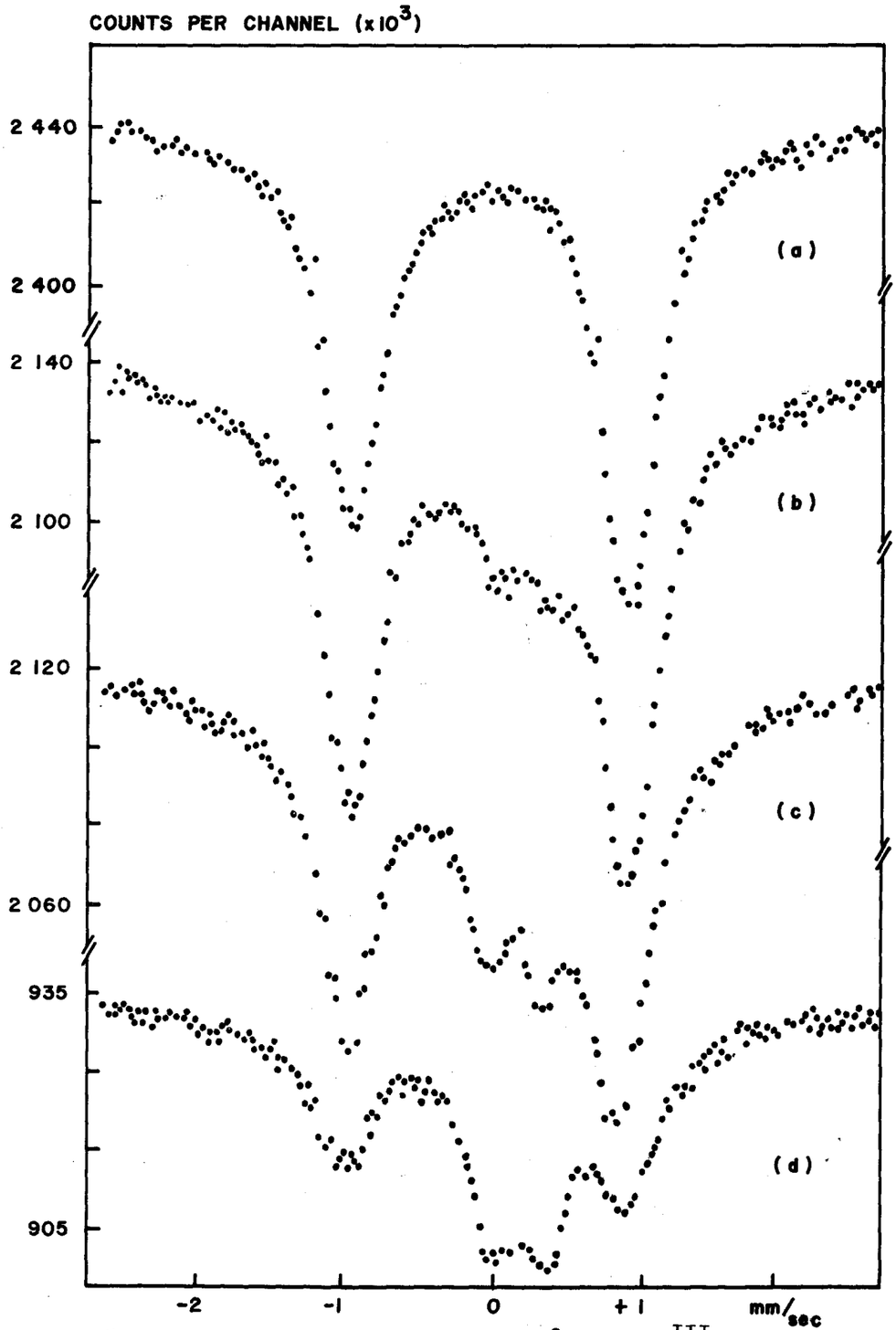

Figure 9 - Mössbauer absorption spectra at 80°K of $|Fe^{III}(dipy)_3|(ClO_4)_3$

(a) unirradiated

(b) irradiated with a dose of 1800 Mrad

(c) irradiated with a dose of 3600 Mrad

(d) irradiated and annealed at 273°K during 3 days.

On the other hand, free radicals are detected in irradiated $\left[Fe^{III}(dipy)_3\right](ClO_4)_3$. This behaviour must be correlated with the irreversibility of the reduction reaction during the annealing. Moreover, the irradiated $\left[Fe^{II}(dipy)_3\right](ClO_4)_2$ did not show any free radicals by ESR, neither an alteration of the Mössbauer spectra.

DISCUSSION

The clear similarity between the emission spectra of the Co chelates and the absorption spectra of the irradiated Fe(III) complexes, illustrated in figures 1 to 4, supports the interpretation of the after-effects of ^{57}Co EC in complex ligand compounds in terms of an autoradiolysis mechanism. The fact that the decayed Fe(III) and Fe(II) species kept essentially the original ligand environment of the ^{57}Co ion suggests that Coulomb fragmentation is a negligible mechanism.

The radiosensitivity of the ligands considered in this work has been established by several authors (19). ESR experiments showed that the most important primary step in the radiolysis involves the formation of $H^{\bullet}$ radicals, which have reducing properties and a high mobility in the solid state (19). The inhibition of the radiolysis of organic ligands in presence of transition metal ions is explained by the participation of the metal cations in a radiolytic protection mechanism through oxidation-reduction processes (18): the remarkably high radiation stability of the organic chelates must be attributed to the fast annihilation of free radicals by redox reactions with the central transition metal ions. On this basis, the following main mechanisms can be proposed to account for the formation of the lower oxidation state after

electron irradiation of these ferric chelates:

$$(1)\ Fe^{III}RH \rightsquigarrow Fe^{III}R^{\bullet} + H^{\bullet} \text{ (primary step)}$$

$$(2)\ Fe^{III}RH + H^{\bullet} \rightleftharpoons Fe^{II}RH + H^{+} \text{ (reduction)}$$

$$(3)\ Fe^{III}R^{\bullet} + H^{\bullet} \longrightarrow Fe^{III}RH \text{ (recombination)}$$

Reactions (1), (2) and (3) are probably much more important than degradation reactions such as

$$(4)\ Fe^{III}R^{\bullet} \rightarrow Fe^{III} + R^{\bullet}$$

and

$$(5)\ Fe^{II}R^{\bullet} \rightarrow Fe^{II} + R^{\bullet}$$

since no evidence for such ionic iron species is found neither by Mössbauer nor by ESR spectroscopy. The redox reaction (2) thus determines the final distribution of the ionic forms in the system. The irreversible behaviour of the Fe(II) - Fe(III) trisdipyridyl system against reduction is correlated to the higher stability of the low-spin ferrous compound. All other chelates investigated in this study present high spin iron ions and the annealing behaviour is determined by the displacement of the equilibrium reaction (2) towards the oxidized form with increasing temperature.

Significant differences probably occur in the mechanism of formation of the reduced species from the EC decay of ^{57}Co and from the radiolysis by external irradiation sources. The irradiation induced during the Auger process corresponds to a very high local dose. In these conditions, the reduction of the transition metal ion can also take place by a direct capture of low-energy electrons originating from the radiolysis of the local molecular environment.

In conclusion, the primary process involved in the after-effects of ^{57}Co EC in complex ligand compounds is the autoradiolysis of the molecular environment and the final distribution of the charge-states of ^{57}Fe can be understood in terms of thermodynamic properties such as the oxidation-reduction potentials established in the considered system.

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