Mössbauer Spectroscopic Studies of the Effect of Anions in the Second Coordination Sphere in the EC-decay

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The ^{57}Fe–Mössbauer emission spectra of ^{57}Co-labelled $[Co(NH_3)_6](NO_3)_3$, $[Co(en)_3](NO_3)_3$, $K_3[Co(CN)_6]$, $K_3[Co(NO_2)_6]$, $[Co(NH_3)_6]_2(C_2O_4)_3 4H_2O$, $[Co(en)_3]_2(C_2O_4)_3 \cdot 9H_2O$, $[Co(NH_3)_6][Fe(CN)_6]$, $[Co(NH_3)_6][Cr(C_2O_4)_3] \cdot 3H_2O$, and $[Co(NH_3)_6][Fe(C_2O_4)_3] \cdot 3H_2O$ sources have been determined. It has been demonstrated that oxalate anions and trisoxalatochromate and trisoxalatoferrate complex anions located outside the first coordination sphere of the decayed atom are still involved in the local radiolytic processes initiated by the EC-decay. The yields of ^{57}Fe species found in the ferrous-charge state were interpreted by using the data of γ-radiolysis and hot-atom chemistry of the $^{59}Co(n,\gamma)^{60}Co$ reaction.

A number of Mössbauer spectroscopic studies have been made of the oxidation state of ^{57}Fe after the EC-decay of ^{57}Co as well as of that of ^{119}Sn after the IT(IC)-decay of ^{119m}Sn. The ^{57}Fe atom produced in the decay suffers a modest recoil, *ca.* 6 eV, and it acquires an average positive charge of 4 or 5 units within 10^{-14} s of its formation becaues of the Auger cascade.[1] The Auger cascade can be invoked as giving rise to charge states more positive than that of the parent ^{57}Co atom, but the factors for the stabilization of the less positive charge state have not been fully understood. One of the explanations of the after-effects of the ^{57}Co EC-decay has been worked out from the difference between the ionic radii of Co^{3+} and Fe^{3+}, which could manifest itself as an internal pressure acting on the decayed atom.[2] We have previously pointed out that a plausible mechanism is the radiolytic process initiated by the Auger process.[3–6] Nath *et al.* have recently suggested the possibility of the fragmentation and the reentry of the degraded ^{57}Fe ion, undergoing excited exchange with a host cobalt molecule.[7] Friedt *et al.* have suggested a similar radiolytic self-decomposition of the molecular environment of the decaying atoms, although they have concluded that the auto-radiolysis is limited to the nearest neighbors of the decayed atom because the electrons emitted during the Auger cascade have a low energy and a short mean path.[8] In the present work, we investigated the effect of anions in the second coordination sphere by comparing the Mössbauer spectra of the ^{57}Co-labelled complex compounds.

Experimental

^{57}Co-labelled Compounds. ^{57}Co-labelled $[Co(NH_3)_6](NO_3)_3$, $[Co(en)_3](NO_3)_3$, $K_3[Co(CN)_6]$, and $K_3[Co(NO_2)_6]$ were prepared from solutions each containing 50 mg of cobalt(II) and about 1 mCi of carrier-free ^{57}Co by following the methods described in Refs. 9, 10, 11, and 12 respectively. ^{57}Co-labelled $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$, $[Co(NH_3)_6][Fe(CN)_6]$, $[Co(NH_3)_6][Cr(C_2O_4)_3] \cdot 3H_2O$, $[Co(NH_3)_6][Fe(C_2O_4)_3] \cdot 3H_2O$, and $[Co(en)_3]_2(C_2O_4)_3 \cdot 9H_2O$ were made from solutions of ^{57}Co-labelled $[Co(NH_3)_6](NO_3)_3$ and $[Co(en)_3](NO_3)_3$ by adding solutions of $K_2C_2O_4 \cdot 2H_2O$, $K_3[Fe(CN)_6]$, $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$, and $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ respectively, purchased or prepared by the methods described in Refs. 13 and 14. The purity was checked by elemental analysis and by X-ray diffraction. All the compounds were found to be at least 98% pure.

Mössbauer Spectroscopic Measurements. The source compounds were kept in a cryostat, and the Mössbauer spectra were measured against an ^{57}Fe-enriched stainless steel absorber moving in a constant acceleration mode at room temperature. Velocity calibrations were carried out by using an ^{57}Fe-enriched iron foil absorber moving against a stationary ^{57}Co(Pt) source at room temperature.

Results and Discussion

Figures 1 to 4 show the Mössbauer spectra of the source compounds measured at 78 K. The spectrum of the ^{57}Co-labelled $K_3[Co(C_2O_4)_3] \cdot 3.5H_2O$ source at

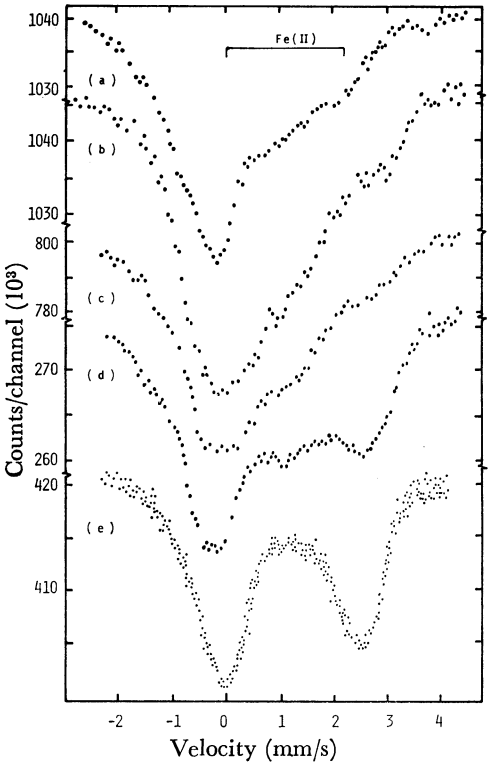

Fig. 1. Mössbauer spectra at 78 K of ^{57}Co-labelled (a) $K_3[Co(CN)_6]$, (b) $K_3[Co(NO_2)_6]$, (c) $[Co(NH_3)_6](NO_3)_3$, and (d) $[Co(en)_3](NO_3)_3$ sources. (e) Spectrum of ^{57}Co-labelled $K_3[Co(C_2O_4)_3] \cdot 3.5H_2O$ source at 93 K reproduced from ref. 15.

93 K is also reproduced in Fig. 1 from Ref. 15 for the sake of comparison. All the velocity scales were normalized with respect to metallic iron. The comparison of the spectra of the $[Co(NH_3)_6](NO_3)_3$, $[Co(en)_3](NO_3)_3$, $K_3[Co(CN)_6]$, and $K_3[Co(NO_2)_6]$ sources with the spectrum of the $K_3[Co(C_2O_4)_3]3.5H_2O$ source clearly shows that the oxalate ligand in the first coordination sphere has the largest effect in reducing the decayed atom, probably because of the decomposition of the oxalate ions to carbon dioxide.

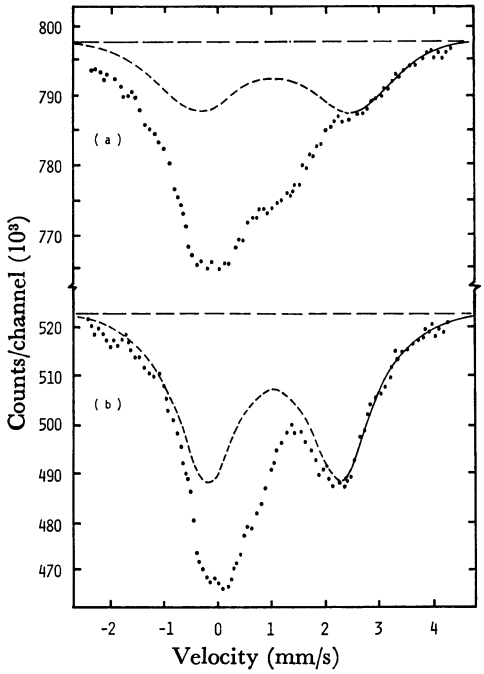

Fig. 2. Mössbauer spectra at 78 K of ^{57}Co-labelled (a) $[Co(NH_3)_6](NO_3)_3$ and (b) $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$ sources. The peak component of ferrous ^{57}Fe species was estimated as indicated in a broken line by using the line shape in the high velocity region ($\gtrsim$2.5 mm/s, indicated in a solid line) where the contribution of ferric species is assumed to be negligible. The yield of ferrous ^{57}Fe species was evaluated from the area under the component and the total area of the spectrum.

As may be seen in Figs. 2 to 4, an increased yield of the ferrous ^{57}Fe species is unambiguously observed in the spectra of $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$, $[Co(en)_3]_2(C_2O_4)_3\cdot 9H_2O$, and $[Co(NH_3)_6][Cr(C_2O_4)_3]\cdot 3H_2O$ and $[Co(NH_3)_6][Fe(C_2O_4)_3]\cdot 3H_2O$ sources compared with the spectra of the $[Co(NH_3)_6](NO_3)_3$, $[Co(en)_3](NO_3)_3$, and $[Co(NH_3)_6][Fe(CN)_6]$ sources respectively, although the yield of the ferrous ^{57}Fe species is lower in those compounds than in $K_3[Co(C_2O_4)_3]\cdot 3.5H_2O$. Since it is known that the water of crystallization has no reducing effect on the oxidation state of ^{57}Fe produced in the after-effect of the EC-decay in a number of ^{57}Co-labelled cobalt compounds,[15-19] it may be concluded that the increased yield of the ferrous ^{57}Fe species is due to the effect of oxalate ions. The higher yield of the ferrous ^{57}Fe species found in $[Co(en)_3](NO_3)_3$ than in $[Co(NH_3)_6](NO_3)_3$ may be explained by assuming a higher probability of bond rupture in the ethylenediamine ligand, thus producing nitrenium

Table 1. Summary of the yield of ferrous ^{57}Fe species produced after EC-decay, the $G(Co^{2+})$ value in γ-radiolysis,[20] and the radiochemical yield of cobaltous ^{60}Co species in the hot-atom chemistry of ^{59}Co(n, γ) ^{60}Co reaction[21]

Compound	Yield of $^{57}Fe^{2+}$ in EC-decay (%)	$G(Co^{2+})$	Yield of $^{60}Co^{2+}$ in ^{59}Co(n, γ) ^{60}Co (%)
$[Co(NH_3)_6](NO_3)_3$	40±1	1.1±0.2	66.7±0.2
$[Co(en)_3](NO_3)_3$	53±1	0.4±0.1	69.4±0.2
$[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$	72±1	2.9±0.2	91.0±0.2
$K_3[Co(C_2O_4)_3]\cdot 3H_2O$	85[15]	11.6±0.2	98.6±0.4

cations (H_2N^+ and $H_2NCH_2CH_2N^+H$), carbonium cations ($H_2NCH_2C^+H_2$, $H_2NCH_2C^+HNH_2$, and $H_2NC^+H_2$), cationic radicals, hydrogen molecules and cations, and electrons which may reduce the decayed atom.

We have reported previously that oxalate anions in the first or second coordination sphere exert some reducing effect both in the radiolysis and in the hot-atom chemistry in the ^{59}Co(n,γ)^{60}Co reaction of cobalt(III) complexes.[20,21] Table 1 summarizes the yields of ferrous ^{57}Fe as evaluated from the spectral area, the $G(Co^{2+})$ value in γ-radiolysis,[20] and the radiochemical yield of ^{60}Co in the hot-atom chemistry.[21] The effect of the oxalate ion on the reduction of the central cation observed in the EC-decay of ^{57}Co qualitatively parallels those data found for the $G(Co^{2+})$ values of γ-ray-irradiated cobalt(III) oxalate complexes and for the radiochemical yields of the divalent ^{60}Co species produced in the (n,γ) reaction. The low $G(Co^{2+})$

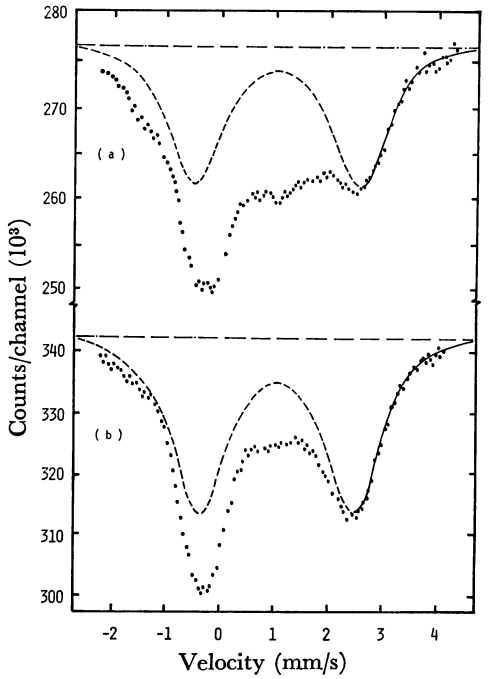

Fig. 3. Mössbauer spectra at 78 K of ^{57}Co-labelled (a) $[Co(en)_3](NO_3)_3$ and (b) $[Co(en)_3]_2(C_2O_4)_3\cdot 9H_2O$ sources. See the figure caption in Fig. 2 for the evaluation of the yield of ferrous ^{57}Fe species.

value found in the γ-radiolysis of $[Co(en)_3](NO_3)_3$ may be ascribed to the low yields of fragmentations, producing nitrenium cations, carbonium cations, cationic radicals, *etc.*, because of the lower LET value of γ-rays compared to those of Auger electrons and recoil ^{60}Co atoms.

Another interesting point concerns the comparison of the spectra of the $[Co(NH_3)_6][Cr(C_2O_4)_3]3H_2O$ and $[Co(NH_3)_6][Fe(C_2O_4)_3]\cdot 3H_2O$ sources. The larger yield of the ^{57}Fe species in the ferrous oxidation state observed in the trisoxalatoferrate(III) source compared to that observed in trisoxalatochromate(III) source may be explained by assuming a higher probability of the decomposition of oxalate ligands into carbon dioxide and electrons induced by the local radiolysis in trisoxalatoferrate. Sugimori and Tsuchihashi have reported that $K_3[Cr(C_2O_3)_3]\cdot 3H_2O$ shows a higher stability against external γ-ray irradiation than does $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$, since the chromous state is much more unstable than is the ferrous state.[22] The $G(CO_2)$ values are evaluated to be 0.9 in the γ-ray irradiation of the trisoxalatochromate(III) and 7.5 in the trisoxalatoferrate(III).

The results indicate that not only the nearest neighbors of the decayed atom (the ligands in the first coordination sphere), but also the next nearest neighbors (the anions or ligands in the second coordination sphere), are involved in determining the oxidation state of the decayed atom in the local radiolytic process initiated by the EC-decay and the Auger effect. The $G(CO_2)$ value reported by Sugimori and Tsuchihashi (9.8) is approximately equal to our previous results of the $G(CO^{2+})$ values evaluated for $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ (11.6). This suggests the following process:

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-;$$

$$2Co(III) + 2e^- \longrightarrow 2Co(II).$$

It is obvious that the decomposition of each oxalate anion can reduce two metal cations from the trivalent to the divalent state. In the ^{57}Co-labelled compounds, however, the concentration of the decaying atom in the host matrix is so small that the electrons produced by each decomposition of oxalate ligands or anions located near the decaying atom may be used to reduce at most only one ^{57}Fe atom to the ferrous state.

As we have previously mentioned, the higher yield of ferrous ^{57}Fe in the EC-decay of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ compared to the yield of stannous ^{119}Sn in the IT(IC)-decay of $K_6Sn_2(C_2O_4)\cdot 4H_2O$ may be ascribed to the difference in the fluorescence yields of iron and tin atom.[4] The fluorescence yield of iron is known to be about 32%. The yield of ferrous ^{57}Fe reported in $K_3[Co(C_2O_4)_3]\cdot 3.5H_2O$ exceeds the value of the Auger yield of iron (68%) by 17%. As long as it is assumed that the yield of ferrous ^{57}Fe depends only upon the nearest neighbors of the decayed atom, the results can be explained in terms of two processes: (1) a direct X-ray radiolysis of oxalate ligands in the trisoxalato ^{57}Fe complex anions which escaped the Auger-electron radiolysis, and (2) an indirect electron transfer through the X-ray radiolysis of the adjacent host trisoxalatocobaltate(III) anions.

The yields of ferrous ^{57}Fe in $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$, $[Co(en)_3]_2(C_2O_4)_3\cdot 9H_2O$, $[Co(NH_3)_6][Cr-$

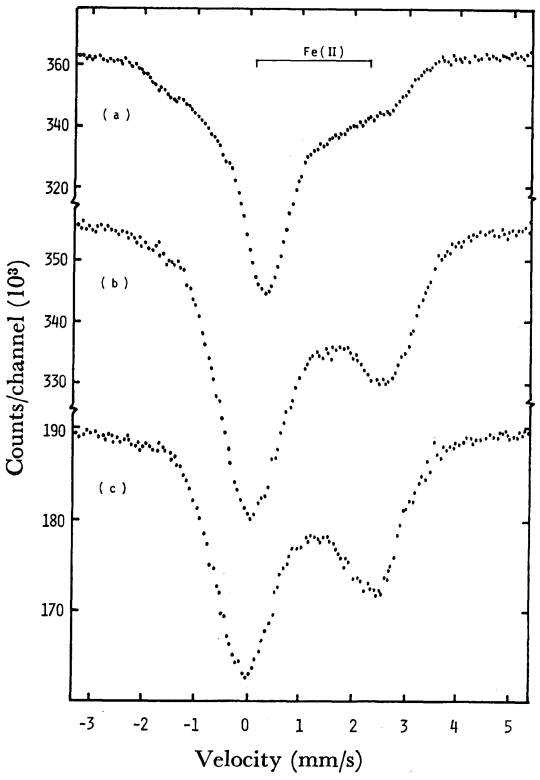

Fig. 4. Mössbauer spectra at 78 K of ^{57}Co-labelled (a) $[Co(NH_3)_6][Fe(CN)_6]$, (b) $[Co(NH_3)_6][Cr(C_2O_4)_3\cdot 3H_2O$, and (c) $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$ sources.

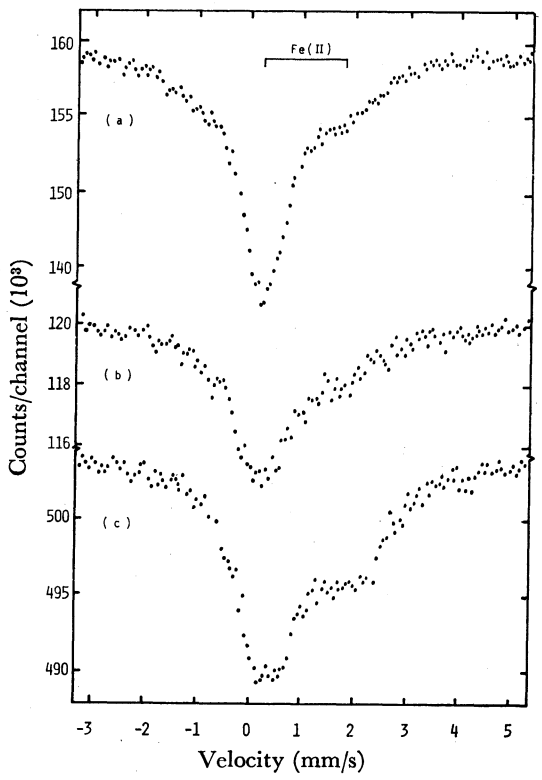

Fig. 5. Mössbauer spectra at 295 K of ^{57}Co-labelled (a) $[Co(NH_3)_6][Fe(CN)_6]$, (b) $[Co(NH_3)_6][Cr(C_2O_4)_3]\cdot 3H_2O$, and (c) $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$ sources.

$(C_2O_4)_3]\cdot 3H_2O$, and $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$ are, however, too high to be explained by the indirect electron transfer through the X-ray radiolysis. The exceptional dissimilarity found in the yield of ferrous ^{57}Fe compared to the $G(Co^{2+})$ value in $[Co(en)_3](NO_3)_3$ may also disprove the X-ray radiolysis mechanism for the interpretation of the main process initiated by the EC- or IT(IC)-decay. It may, therefore, be concluded that Auger electrons emitted from the decayed atom decompose oxalate ions outside the first coordination sphere or that the Auger process gives rise to an excitation-induced decomposition of the oxalate ions and that electrons thus produced are then transfered to the decayed atom, thus stabilizing a reduced oxidation state during the nuclear life-time of the first excited level of the Mössbauer nucleus.

These conclusions are consistent with our previous interpretation derived from the studies of $^{57}Co(acac)_3$ doped into a number of trisacetylacetonato complexes, where a remarkable dependence of the yield of ferrous ^{57}Fe is found on the kind of surrounding host matrix. A comparison of the spectrum of ^{57}Co-labelled $K_3[Co(CN)_6]$ with that of $[Co(NH_3)_6][Fe(CN)_6]$ does not show any positive evidence for the excited exchange of ^{57}Fe produced from the EC-decay of ^{57}Co with iron(III) atoms of hexacyanato complex anions, although a minor possibility of this can not be denied. The peak component assigned to the ferrous ^{57}Fe species decreases relative to that of the ferric species at room temperature, especially in the cases of the $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$, $[Co(en)_3]_2(C_2O_4)_3\cdot 9H_2O$, $[Co(NH_3)_6][Cr(C_2O_4)_3]\cdot 3H_2O$, and $[Co(NH_3)_6][Fe(C_2O_4)_3]\cdot 3H_2O$ sources. Some typical spectra observed at 295 K are shown in Fig. 5. This suggests that the ferrous species have lower recoil-free fractions, since they are located in disturbed or thermally excited environments.

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