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MÖSSBAUER SPECTROSCOPIC STUDIES OF THE EC-AFTER EFFECT IN ^{57}Co-LABELLED $[Co(NH_3)_6][Fe(CN)_6]$, $[Co(NH_3)_6][Cr(C_2O_4)_3]3H_2O$, AND $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$

Hirotoshi SANO and Toshiaki OHNUMA

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University

Fukazawa, Setagaya, Tokyo 158

It has been demonstrated that oxalate ligands of trisoxalatochromate(III) and trisoxalatoferrate(III) 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 ferrous charge state were interpreted by using radiolytical data on potassium trisoxalatochromate(III) and trisoxalatoferrate(III).

The observation of chemical after-effects associated to the EC-decay of ^{57}Co has been reported in a number of ^{57}Co-labelled compounds and ^{57}Co-doped materials. These after-effects have been ascribed to the radiolytical process of the local enviroment of the decaying atoms induced by the low energy Auger electrons and X-rays.$^{1-6)}$ We have demonstrated previously that the surrounding matrix of an EC-decayed ^{57}Co(acac)$_3$ moiety is involved in the local radiolytic processes and that the fate of the produced ^{57}Fe atoms is determined not only by the radiolytical properties of the nearest ligands of the decaying atom but also by those of the outer chemical species.$^{2)}$ Friedt *et al.* have concluded, however, that the autoradiolysis is limited to the nearest neighbors of the decayed atom because that electrons and X-rays emitted during the Auger cascade have a low energy and a short mean path, based on their studies of ^{57}Co-labelled Co(acac)$_3$ and some other cobalt compounds.$^{4-6)}$ In the present work the chemical after-effects of the EC-decay of ^{57}Co in hexamminecobalt(III) trisoxalatochromate(III) and trisoxalatoferrate(III) are compared with those of hexamminecobalt(III) nitrate and hexacyanatoferrate(III) in order to elucidate the extent of the region involved in the autoradiolysis and also to justify the validity of the radiolytical mechanism in this zone.

^{57}Co-labelled $[Co(NH_3)_6](NO_3)_3$ source was prepared from a solution containing 50 mg of cobalt(II) and about 1 mCi of carrier-free ^{57}Co by following the method described in ref. 7. ^{57}Co-labelled $[Co(NH_3)_6][Fe(CN)_6]$, $[Co(NH_3)_6][Cr(C_2O_4)_3]3H_2O$, and $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$ sources were made from a solution of ^{57}Co-labelled $[Co(NH_3)_6](NO_3)_3$ by adding solutions of $K_3[Fe(CN)_6]$, $K_3[Cr(C_2O_4)_3]3H_2O$, and $K_3[Fe(C_2O_4)_3]3H_2O$ purchased or prepared by the methods described in refs. 8 and 9. The purity was checked by elemental analysis and X-ray diffraction. All the compounds were at least 98% pure. Mössbauer spectra of the sources were measured against an ^{57}Fe-enriched stainless steel absorber moving in a constant acceleration mode at room

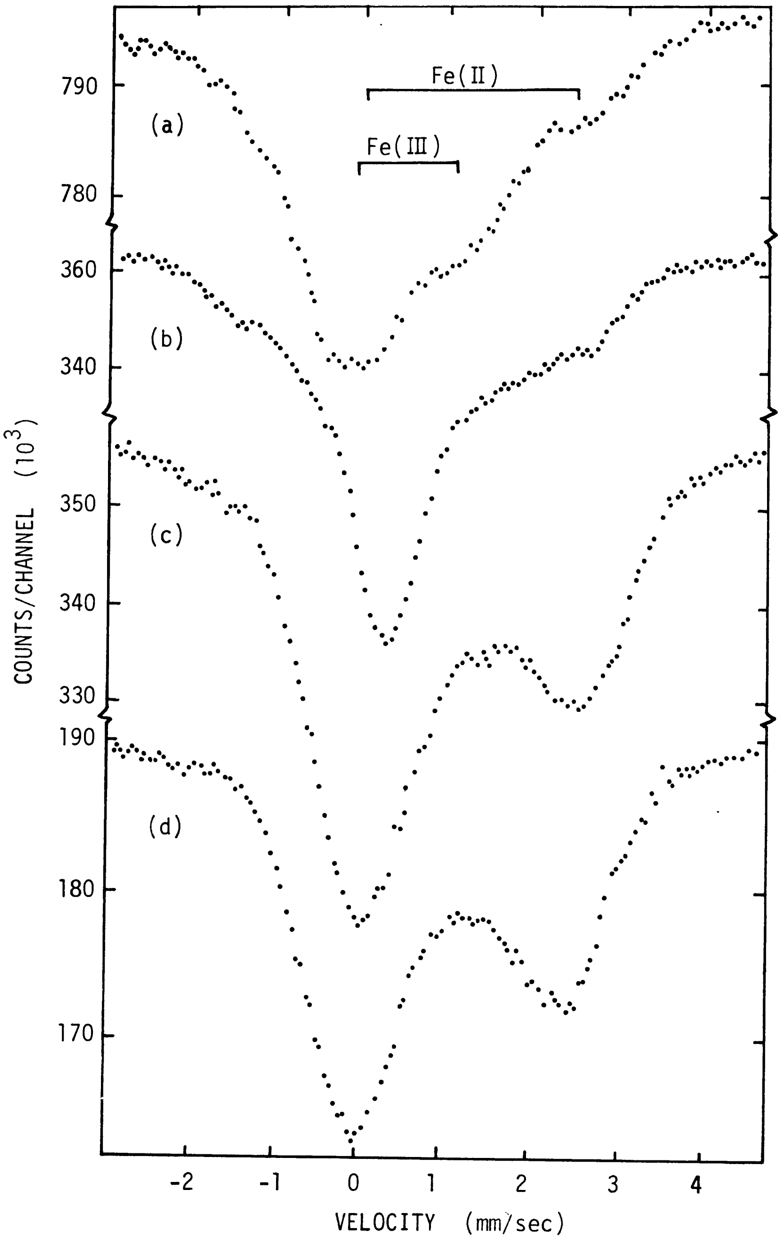

Fig. 1. Mössbauer spectra at 78 K of ^{57}Co-labelled (a) $[Co(NH_3)_6](NO_3)_3$, (b) $[Co(NH_3)_6][Fe(CN)_6]$, (c) $[Co(NH_3)_6][Cr(C_2O_4)_3]3H_2O$, and (d) $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$ sources. All the velocity scales were normalized with respect to metallic iron.

temperature. Typical Mössbauer spectra are shown in Figs. 1 and 2. The spectra may be decomposed into two doublets ascribed to ferrous and ferric species, respectively.

An increased reducing effect of the outer anions is clearly observed in the spectra of $[Co(NH_3)_6][Cr(C_2O_4)_3]3H_2O$ and $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$ sources compared with in the spectra of $[Co(NH_3)_6](NO_3)_3$ and $[Co(NH_3)_6][Fe(CN)_6]$ sources. Since it is known that water of crystallization has little effect on the reduction of ^{57}Fe in the after-effect of EC-decay in a number of ^{57}Co-labelled cobalt compounds,[10-12] it may be concluded that the increased yield of ferrous ^{57}Fe species is due to the effect of trisoxalato complex anions, *i. e.*, the oxalate ligands not coordinated to

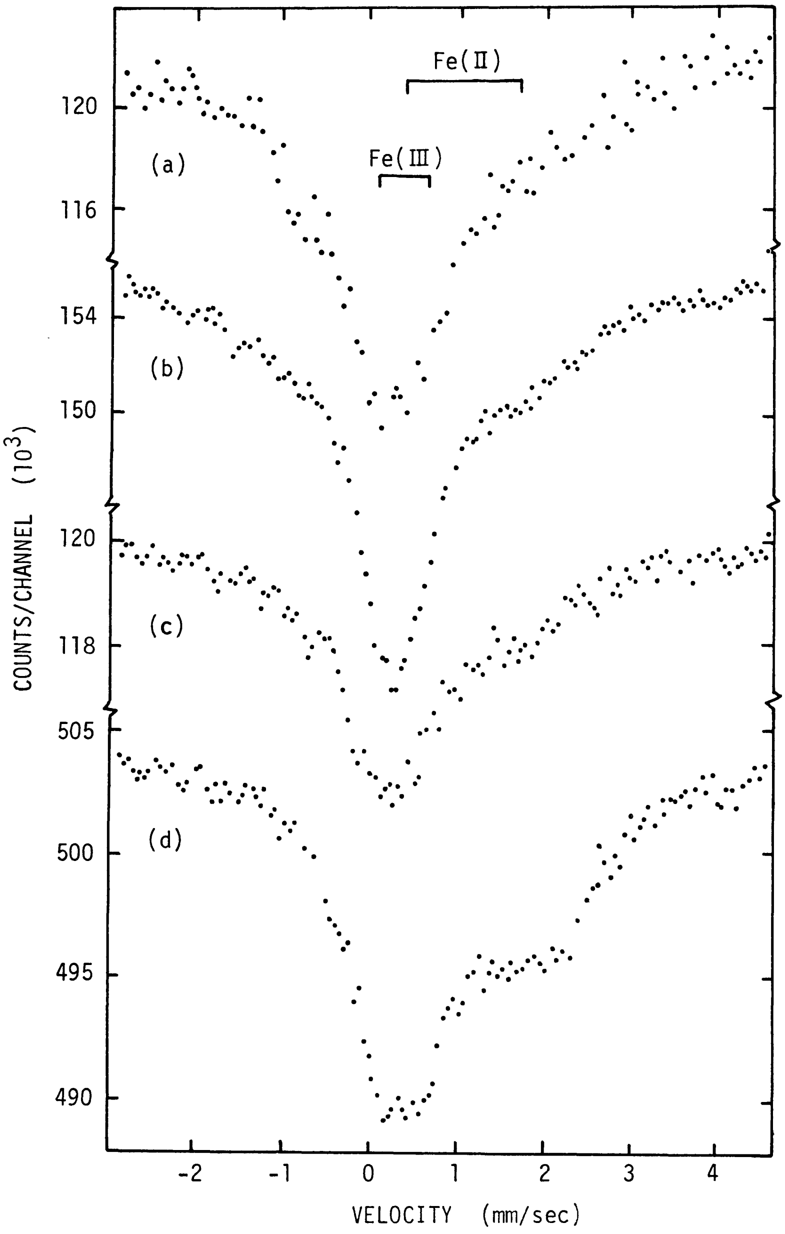

Fig. 2. Mössbauer spectra at 295 K of ^{57}Co-labelled (a) $[Co(NH_3)_6](NO_3)_3$, (b) $[Co(NH_3)_6][Fe(CN)_6]$, (c) $[Co(NH_3)_6][Cr(C_2O_4)_3]3H_2O$, and (d) $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$ sources. All the velocity scales were normalized with respect to metallic iron.

the decayed atom but located outside the first coordination sphere of the decayed atom are still involved in the radiolytic processes initiated by the EC-decay. In the spectra observed at room temperature, the peak component ascribed to ferrous species decreases relative to that of ferric species in each source compounds. This suggests that the ferrous species have lower recoil-free fractions since they are located in disturbed or thermally excited environments.

Another interesting point concerns the comparison of the spectra of $[Co(NH_3)_6][Cr(C_2O_4)_3]3H_2O$ and $[Co(NH_3)_6][Fe(C_2O_4)_3]3H_2O$ sources. The larger yield of ^{57}Fe species in ferrous oxidation state observed in trisoxalatoferrate(III) compared to in trisoxalatochromate(III) source may be explained by assuming the higher probability of decomposition of oxalate ligands into carbon dioxide and electrons induced by the local radiolysis in trisoxalatoferrate(III). Sugimori and Tsuchihashi have reported that $K_3[Cr(C_2O_4)_3]3H_2O$ shows higher stability against external γ-ray irradiation compared to $K_3[Fe(C_2O_4)_3]3H_2O$, since chromous state is much more unstable than is ferrous state.[13] 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 chemical species outside the first coordination sphere of the decayed atom can not be ignored if they have a considerable effect in the radiolytical process. These conclusions are consistent with our previous interpretation derived from the studies of $^{57}Co(acac)_3$ doped into a number of trisacetylacetonato complexes.

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