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Studies of Matrix Effects on ^{57}Co-Labelled Tris(β-diketonato)cobalt(III) by Means of Mössbauer Spectroscopy

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Synopsis. The emission Mössbauer spectra at 78 K of ^{57}Co-labelled Co(dbm)$_3$ (dbm=dibenzoylmethanato) dispersed in 2-methyltetrahydrofuran, or of ^{57}Co-labelled Co(acac)$_3$ (acac=acetylacetonato) dispersed in a mixed medium of oxalic acid and polystyrene, give no appreciable magnetic hyperfine structure (hfs), while those of ^{57}Co-labelled Co(acac)$_3$ dispersed in polystyrene and ^{57}Co-labelled crystalline Co(dbm)$_3$ give a magnetic hfs. The results indicate that the local radiolysis of EC-decay involves not only the labelled species itself, but also the neighbouring host matrix.

A number of emission Mössbauer spectroscopic studies of the ^{57}Co-labelled diamagnetic cobalt(III) compounds have shown practically no magnetic hyperfine structure (hfs), although the decayed ^{57}Fe(III)-paramagnetic species are considered to be magnetically diluted in a diamagnetic host.[1–5] The results are indicated in terms of an enhanced spin-spin interaction between the unpaired electrons of the ^{57}Fe and paramagnetic species produced through the EC-decay in the vicinity of ^{57}Fe. In our previous work,[6–7] however, a well-resolved paramagnetic hfs was found in the emission Mössbauer spectra of ^{57}Co-labelled tris(dibenzoylmethanato)cobalt(III), Co(dbm)$_3$, at 4.2 K. The results are explained from the viewpoint of the reduced formation of paramagnetic species (mainly organic radicals) in the vicinity of the decayed ^{57}Fe. It was also reported that the radical formation in the EC-Auger after-effects is small in such compounds that have ligands with a π-conjugated system and that the results are closely related to the radiolytic stability of the labelled compounds.[8]

In the present paper, we examined the emission Mössbauer spectra of the dispersion systems of ^{57}Co-labelled compound in order to get information about the matrix effects in the EC-decay. The dispersion systems of β-diketonates of cobalt(III) used are ^{57}Co-labelled Co(acac)$_3$ dispersed in a mixed medium of oxalic acid and polystyrene, and Co(dbm)$_3$ in 2-methyltetrahydrofuran.

Experimental

Preparation of Source Materials. ^{57}Co-labelled Co(dbm)$_3$ was prepared by following the method described previously.[7] The labelled complex was dissolved in 2-methyltetrahydrofuran, which is known to exist in vitreous structures when it is rapidly cooled. The solution was poured into a cell specially designed for the emission Mössbauer measurement. The cell was set in a cryostat and cooled by immersing it in liquid nitrogen as rapidly as possible.

A 100-mg portion of polystyrene and about 10 mg of Co(acac)$_3$ containing the ^{57}Co-labelled compound were dissolved into tetrahydrofuran, and then a 5-mg portion of oxalic acid was added to the mixture. Oxalic-acid crystals were dissolved on heating, after which the solution was allowed to stand in the air. The homogeneous dispersion of the sample prepared in the cold run was checked by X-ray diffractometry.

Measurement of Mössbauer Spectra. The emission Mössbauer spectra of the source materials at 78 K were measured against an ^{57}Fe-enriched stainless-steel absorber moving in a mode of constant acceleration. Velocity calibration was carried out by normalizing to iron metal.

Results and Discussion

The emission Mössbauer spectra at 78 K of ^{57}Co-labelled Co(acac)$_3$ dispersed in a mixed medium of oxalic acid and polystyrene give practically no magnetic hfs, as is shown in Fig. 1—a; they are similar to those found for pure crystalline ^{57}Co-labelled Co(acac)$_3$.[4] When the results are compared with the emission spectrum of ^{57}Co-labelled Co(acac)$_3$ dispersed in polystyrene,[7] they show that the oxalic acid plays a role in accelerating the rate of relaxation.

The emission Mössbauer spectrum at 78 K of ^{57}Co-labelled Co(dbm)$_3$ dispersed in 2-methyltetrahydrofuran is shown in Fig. 1—b. The magnetic hfs found in pure crystalline ^{57}Co-labelled Co(dbm)$_3$[6–7] decreased drastically in the present system.

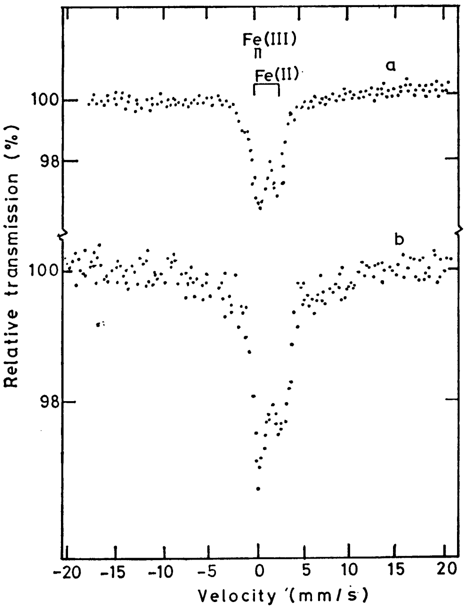

Fig. 1. Emission Mössbauer spectra at 78 K of ^{57}Co-labelled tris(acetylacetonato)cobalt(III) dispersed in a mixed medium of oxalic acid and polystyrene(a), and ^{57}Co-labelled tris(dibenzoylmethanato)cobalt(III) dispersed in 2-methyltetrahydrofuran(b).

We have explained that the appearance or disappearance of magnetic hfs in the emission Mössbauer spectrum of a cobalt(III) compound depends on the radiolytic stability of the source compounds; *i.e.* a compound which is stable against the local radiolysis of EC-decay gives a magnetic hfs.[8] The acceleration of the relaxation rate (or the disappearance of the magnetic hfs) in the present dispersion system can be explained by assuming an enhanced spin-spin interaction due to the increased radiolytic production of paramagnetic radicals in the vicinty of the decayed ^{57}Fe(III). Probably the radiolysis may occur in a dispersion medium as well as in a source compound, and it may be reasonable to conclude, from the results of the present experiment, that the radiation stability of a dispersion medium will contribute to change the rate of relaxation.

Although the relaxation rate is also enhanced by the spin-lattice interaction, this will make a minor contribution since the local heating due to the recoil energy of EC-decay should spread over the surrounding atoms by thermal diffusion in a much shorter time than the lifetime of the Mössbauer nuclear level.

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