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Mössbauer Spectroscopic Studies of the Chemical Effects Associated with ^{57}Co(Electron Capture)^{57}Fe Decay in Tris-β-diketonatocobalt(III) Compounds

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Magnetic hyperfine structures (hfs) were found in the absorption Mössbauer spectra at 78 K of a paramagnetic iron(III) complex diluted in a diamagnetic cobalt(III) or aluminium(III) complex, such as ^{57}Fe(acac)$_3$ in Co(acac)$_3$, ^{57}Fe(oxin)$_3$ in Al(oxin)$_3$, and ^{57}Fe(dbm)$_3$ in Co(dbm)$_3$ (acac=acetylacetonato, oxin=8-quinolinolato, and dbm=dibenzoylmethanato), showing that the magnetic hfs is caused by the spin-spin relaxation through the surrounding diamagnetic species. In the emission Mössbauer experiments, magnetic hfs was observed at 78 K in ^{57}Co-labelled Co(dbm)$_3$, Co(oxin)$_3$, and polystyrene-diluted Co(acac)$_3$, while it was not observed in ^{57}Co-labelled Co(acac)$_3$ and Co(dpm)$_3$ (dpm=dipivaloylmethanato). The former possess π-conjugated systems to a greater extent than the latter, either in the ligands or in the vicinity of the ^{57}Co-labelled Co(III) species. These results were explained in terms of the radiolytic stabilities of the matrices as well as those of ^{57}Co-labelled compounds by showing that the paramagnetic radicals produced in a diamagnetic matrix quench the magnetic hfs because of the increased spin-spin interaction, as a consequence of the local radiolysis by EC-decay.

Emission Mössbauer spectroscopic studies have provided us with important information on the chemical fate of the decayed atom in a solid. We have ourselves reported on the chemical effects in the ^{57}Co(EC)^{57}Fe decay process in cobalt(III) coordination compounds by applying the technique. It was observed that the decayed ^{57}Fe species exist in one or more anomalous charge states within the lifetime of the nuclear excited level of ^{57}Fe.1–3) It was also found that the yield of anomalous species, the high-spin ^{57}Fe(II) species, produced after the EC-decay and the subsequent Auger process is quite high in the ^{57}Co(III) coordination compounds containing the oxalato ligands or the oxalate anions, such as in $K_3[Co(C_2O_4)_3]\cdot 3H_2O$1) and $[Co(NH_3)_6]_2(C_2O_4)_3$.3) In order to explain the results, the local radiolytic process was proposed on the basis of absorption Mössbauer experiments in the γ-ray-irradiated $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$.4) In the local radiolytic process, the radical formation was assumed in the first stage (*e.g.*, $CO_2^{\overline{\cdot}}$ from an oxalato ligand or an oxalate anion). Then, the radical may be stabilized by releasing an electron (*e.g.*, $CO_2^{\overline{\cdot}}$ into CO_2+e^-), which results in the reduction of the ^{57}Fe(III) species, enhancing the yield of the ^{57}Fe(II) species. On the other hand, it has been reported that the magnetic hyperfine structure (hfs) caused by spin-spin relaxation was found in the absorption Mössbauer spectra of high-spin iron(III) (S=5/2) coordination compounds diluted in diamagnetic compounds—for example, in the spectra of tris(acetylacetonato)iron(III), Fe(acac)$_3$, diluted in Co(acac)$_3$2) or Al(acac)$_3$5). However, in the emission Mössbauer spectra of ^{57}Co-labelled diamagnetic cobalt(III) coordination compounds, little or no magnetic hfs has been observed at the temperature of the absorption experiments, although the decayed ^{57}Fe(III) species remain in magnetically diluted environments of diamagnetic Co(III) compounds. The discrepancy between the results of the absorption and emission Mössbauer spectroscopic studies can be explained by assuming that the enhanced spin-spin interaction between ^{57}Fe atoms and the radicals produced in the local radiolysis through the EC and Auger processes should quench the magnetic hfs in the emission Mössbauer spectra of ^{57}Co-labelled cobalt(III) coordination compounds.

In the present paper, the emission Mössbauer spectroscopic studies of various tris(β-diketonato)cobalt(III) compounds are described in order to clarify the relation of the magnetic hfs, *i.e.*, the radical formation associated with the ^{57}Co(EC)^{57}Fe decay process, with the radiolytic property of the ligands or matrices in the vicinity of ^{57}Co-labelled compounds.

Experimental

Preparation of Materials Used. The mixed crystals of tris(8-quinolinolato)^{57}Fe(III), ^{57}Fe(oxin)$_3$, and Al(oxin)$_3$ were prepared by the co-precipitation method. The molar fraction of ^{57}Fe(oxin)$_3$ was 0.03; the homogeneity of Fe(oxin)$_3$ diluted in Al(oxin)$_3$ was confirmed by X-ray diffraction analysis to be as shown in Fig. 1, where the X-ray powder patterns of Fe(oxin)$_3$ and Al(oxin)$_3$ are different from each other and where the pattern of the mixed crystals shows that of Al(oxin)$_3$, but not Fe(oxin)$_3$, though the mixture of Fe(oxin)$_3$ and Al(oxin)$_3$ with the same molar fraction shows a small but clear contribution of Fe(oxin)$_3$ in the

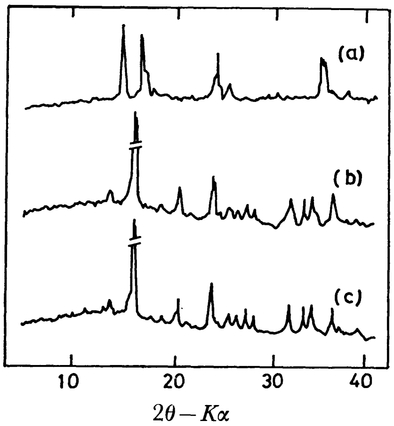

Fig. 1. X-Ray diffraction patterns of a) Fe(oxin)$_3$, b) Al(oxin)$_3$, and c) 3% mol (^{57}Fe-Al)(oxin)$_3$.

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diffraction pattern. The mixed crystals of tris(dibenzoylmethanato)^{57}Fe(III), ^{57}Fe(dbm)$_3$, and Co(dbm)$_3$ were prepared by the freeze-dry method, in which the molar fraction of ^{57}Fe(dbm)$_3$ was 0.03.

The ^{57}Co-labelled Co(acac)$_3$ was prepared according to the literature.[6] The mixture of $CoCO_3$ containing *ca.* 1.0 mCi of ^{57}Co and acetylacetone was refluxed at 90 to 100 °C by adding 10% H_2O_2. When the resultant green solution was cooled in an ice-bath, green crystals were deposited. The crystals were filtered and washed with water and methanol. The crude crystals were recrystallized from a benzene–hexane solution.

The ^{57}Co-labelled tris(dipivaloylmethanato)Co(III) complex, Co(dpm)$_3$, was prepared as follows: A mixture of $CoCO_3$ containing *ca.* 1.0 mCi of ^{57}Co and dipivaloylmethane was refluxed in ethanol by adding 10% H_2O_2. The crude green crystals thus separated were washed with ethanol. The resultant ^{57}Co(dpm)$_3$ was purified by the recrystallization of the benzene–hexane solution.

The ^{57}Co(dbm)$_3$ was prepared by an ordinary method. A mixture of $CoCO_3$ containing 1.0 mCi of ^{57}Co and dibenzoylmethane was strongly refluxed in ethanol by adding 10% H_2O_2. The crude product in the solution was filtered and washed with ethanol. The purification of ^{57}Co(dbm)$_3$ was carried out by alumina-column chromatography in a benzene solution.

The ^{57}Co-labelled Co(oxin)$_3$ was prepared according to Ablob's method;[7] that is, $CoCl_2 \cdot 6H_2O$ containing 1.0 mCi of ^{57}Co and 8-quinolinol were dissolved in ethanol, and the product was precipitated and collected. The purification was carried out by recrystallization.

The ^{57}Co(acac)$_3$ diluted in polystyrene was prepared as follows. The ^{57}Co(acac)$_3$ prepared with 5 mg of $CoCO_3$ containing 1.0 mCi of ^{57}Co was dissolved in benzene, to which a few hundred miligrams of polystyrene were added and dissolved homogeneously. The highly viscous solution was dried in air. The homogeneity of the Co(acac)$_3$ diluted in polystyrene was confirmed by X-ray diffraction analysis in cold experiments. The diffraction pattern of Co(acac)$_3$ diluted in polystyrene showed an amorphous state, while that of the mixture of Co(acac)$_3$ and polystyrene with the same contents as the diluted samples showed the peaks of both the crystalline Co(acac)$_3$ and the amorphous pattern of polystyrene.

The chemical structures of the metal(III) coordination compounds concerned in the present work are illustrated in Fig. 2.

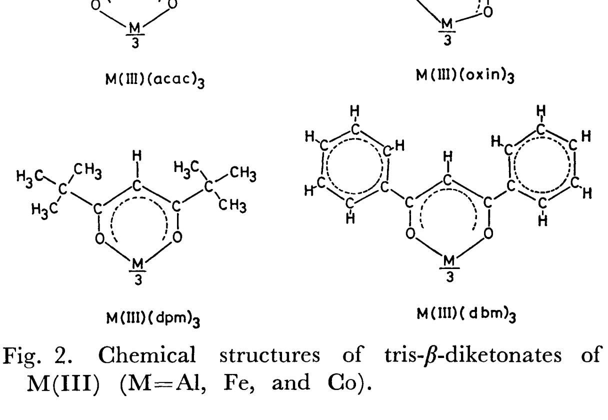

Fig. 2. Chemical structures of tris-β-diketonates of M(III) (M=Al, Fe, and Co).

Measurement of Mössbauer Spectra. The absorption Mössbauer spectra of the samples were measured at 78 K against a ^{57}Co(Pt) source moving in a mode of a constant-acceleration. Since all the emission Mössbauer spectra of the source materials kept at various temperatures (4.2 to 198 K) were measured against a moving ^{57}Fe-enriched stainless-steel as an absorber, both the emission and absorption spectra shown in Figs. 3—7 can be directly compared with each other. Velocity calibration was carried out by normalizing to iron metal in both the absorption and emission experiments.

Results

The absorption Mössbauer spectra at 78 K of ^{57}Fe(oxin)$_3$ diluted in diamagnetic Al(oxin)$_3$, ^{57}Fe(acac)$_3$ diluted in Co(acac)$_3$, and ^{57}Fe(dbm)$_3$ diluted in Co(dbm)$_3$ are shown in Figs. 3 (a), (b), and (c) respectively. The magnetic hfs is found in all the spectra of the mixed crystals at 78 K.

The emission Mössbauer spectra of crystalline ^{57}Co(dpm)$_3$, ^{57}Co(acac)$_3$, ^{57}Co(oxin)$_3$, and ^{57}Co(dbm)$_3$ at 78 K are shown in Figs. 4 (a), (b), (c), and (d) respectively. The magnetic hfs is observed in the spectra of ^{57}Co(oxin)$_3$ and ^{57}Co(dbm)$_3$, while almost no magnetic hfs is found in those of ^{57}Co(acac)$_3$ and ^{57}Co(dpm)$_3$ at 78 K. The emission Mössbauer spectra of ^{57}Co(dpm)$_3$, ^{57}Co(oxin)$_3$, and ^{57}Co(dbm)$_3$ at 4.2 K are shown in Figs. 5 (a), (b), and (c) respectively. The spectra of ^{57}Co(acac)$_3$ at 78 K and 4.2 K were reported by Nath *et al.*;[8] they are very similar to those of ^{57}Co(dpm)$_3$ shown in Figs. 4 and 5. The temperature-dependence of the emission Mössbauer spectrum is demonstrated for ^{57}Co(dbm)$_3$ in Fig. 6. The intensity of the magnetic hfs is found to increase with the decrease in the temperature. The emission

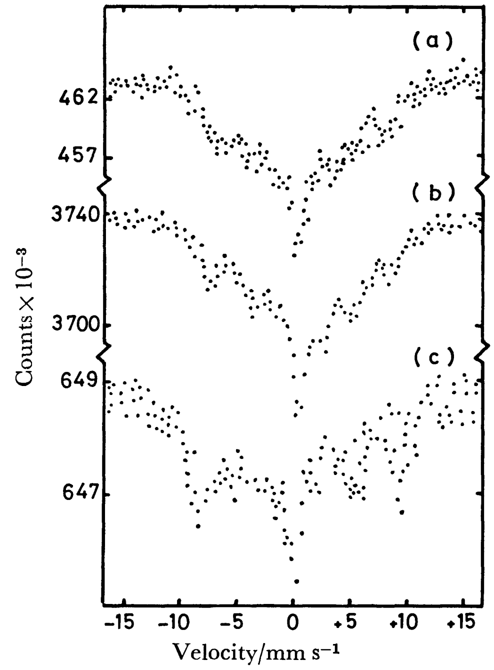

Fig. 3. Absorption Mössbauer spectra at 78 K of a) ^{57}Fe(oxin)$_3$ diluted in Al(oxin)$_3$, b) ^{57}Fe(acac)$_3$ diluted in Co(acac)$_3$, and c) ^{57}Fe(dbm)$_3$ diluted in Co(dbm)$_3$.

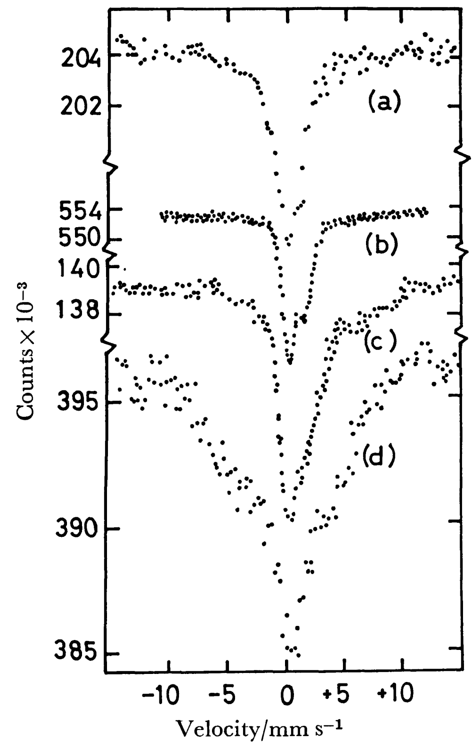

Fig. 4. Emission Mössbauer spectra at 78 K of a) ^{57}Co(dpm)$_3$, b) ^{57}Co(acac)$_3$, c) ^{57}Co(oxin)$_3$, and d) ^{57}Co(dbm)$_3$.

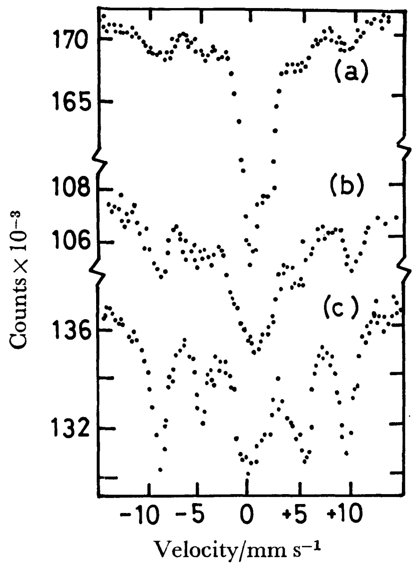

Fig. 5. Emission Mössbauer spectra at 4.2 K of a) ^{57}Co(dpm)$_3$, b) ^{57}Co(oxin)$_3$, and c) ^{57}Co(dbm)$_3$.

spectrum at 78 K of ^{57}Co(acac)$_3$ diluted in polystyrene is shown in Fig. 7, while the crystalline ^{57}Co(acac)$_3$ is shown in Fig. 4 (b). The magnetic hfs is clearly found in the diluted sample.

Discussion

The magnetic hfs in the Mössbauer spectrum is known to arise from the interaction between the internal magnetic field caused by the electron-spin and the magnetic moment of the Mössbauer nucleus. In

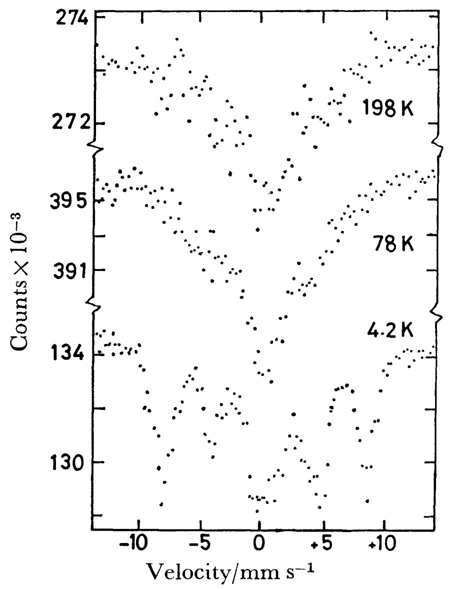

Fig. 6. Temperature-dependence of emission Mössbauer spectra for ^{57}Co(dbm)$_3$.

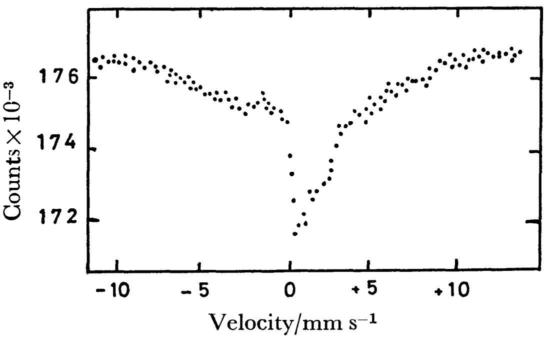

Fig. 7. Emission Mössbauer spectrum at 78 K of ^{57}Co(acac)$_3$ diluted in polystyrene.

many paramagnetic iron compounds, however, the magnetic hfs is not observed in the absorption spectrum except at very low temperatures, because the internal magnetic field fluctuates in direction through the spin-spin and spin-lattice interactions with the surrounding atoms and/or molecules. Paramagnetic iron compounds diluted in diamagnetic compounds show the magnetic hfs at higher temperatures because of the decreased spin-spin interaction in the diluent diamagnetic compound. It is also known that a magnetic hfs of a small magnitude can be observed in the absorption spectra of the paramagnetic iron compounds with a large molecular size, as has been demonstrated by Wignall for Fe(dbm)$_3$ at 1.8 K.[9] We have previously reported that paramagnetic Fe(acac)$_3$ diluted in Co(acac)$_3$ shows the magnetic hfs in the absorption spectra at 78 to 230 K, but not Fe(acac)$_3$ diluted in paramagnetic Mn(acac)$_3$ or Cr(acac)$_3$ at the same temperature.[2]

In the present study, the absorption spectra at 78 K of paramagnetic ^{57}Fe(oxin)$_3$ diluted in diamagnetic Al(oxin)$_3$ and ^{57}Fe(dbm)$_3$ diluted in diamagnetic Co(dbm)$_3$ gave the magnetic hfs as well. As is known, the magnetic hfs is not clearly observed in the emission Mössbauer spectrum at 78 K in most ^{57}Co-labelled cobalt(III) coordination compounds, such as hexammine cobalt(III), hexacyanocobaltate(III), tris(oxalato)-cobaltate(III), and tris(acetylacetonato)cobalt(III). When paramagnetic ^{57}Fe species produced through the EC-decay remain in environments diluted magnetically by diamagnetic cobalt(III) host compounds, the magnetic hfs might be expected to be observed to the same extent as in the paramagnetic Fe(III) species diluted in diamagnetic Co(III) compounds. In order to explain the experimental results (*i.e.*, that little or no magnetic hfs has been observed in most emission spectra at 78 K of the ^{57}Co-labelled cobalt(III) compounds), we have proposed that some species with an electron-spin should be formed in the vicinity of the decayed ^{57}Fe atoms and that the paramagnetic species with an electron spin should suppress the magnetic hfs through the spin-spin interaction with the paramagnetic ^{57}Fe species. The paramagnetic species were assumed to be radicals produced through the local radiolysis in the EC-decay and the subsequent Auger process.

As may be seen in Fig. 4, the magnetic hfs is observed in the emission spectra at 78 K in the source compounds, ^{57}Co(oxin)$_3$ and ^{57}Co(dbm)$_3$. The emission spectra at 4.2 K of these source compounds show the magnetic hfs to a much greater degree than at 78 K. The spectrum of ^{57}Co(dpm)$_3$ also shows the magnetic hfs at 4.2 K, but the intensity is apparently lower than those found in ^{57}Co(dbm)$_3$ and ^{57}Co(oxin)$_3$. The spectrum of ^{57}Co(acac)$_3$ at the temperature of liquid helium reported by Nath *et al.*[8] is very similar to that of ^{57}Co(dpm)$_3$. The intensities of the magnetic hfs at 4.2 K and 78 K decrease in the following order: $^{57}\text{Co(dbm)}_3 > {}^{57}\text{Co(oxin)}_3 > {}^{57}\text{Co(dpm)}_3 \fallingdotseq {}^{57}\text{Co(acac)}_3$. The former two compounds have aromatic π-conjugated systems in the ligands, while the latter two compounds have no such aromatic system, as may be seen in Fig. 2. The appearance of the magnetic hfs might be related to the chemical structure of the source compound, especially to whether or not the source compound possesses π-conjugated systems in the ligands. Furthermore, the appearance of the magnetic hfs in the emission spectrum at 78 K of ^{57}Co-(acac)$_3$ diluted in polystyrene shown in Fig. 7 can be explained in a similar way. The fact that fewer of the paramagnetic radicals are produced in the diluted sample of ^{57}Co(acac)$_3$ in polystyrene than in the neat crystalline ^{57}Co(acac)$_3$ may be ascribed to the effects of the many phenyl groups involved in polystyrene. It is well known in radiation chemistry that the radiolytic stability of compounds with π-conjugated systems is much larger than that of compounds with only σ-bond systems. The G-values of the free ion of various organic compounds in 2 MeV X-ray radiolysis were reported by Schmidt and Allen,[10] who showed that those values in aromatics and olefines are much smaller than in alkanes. From the radiation-chemical point of view, it may be concluded that the appearance of the magnetic hfs in the emission Mössbauer spectrum of a ^{57}Co-labelled cobalt(III) coordination compound proves the radical-formation hypothesis in the local radiolysis through the EC-Auger process.

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