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Mössbauer Spectroscopic Studies of the Correlation between Molecular Structure and Sign of Quadrupole Splitting in Tris(β-diketonato)-iron(III) Complexes Utilizing Paramagnetic Relaxation Effects

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The change of the Mössbauer line shape with the paramagnetic relaxation time was studied in several tris(β-diketonato)iron(III) complexes to determine the sign of the quadrupole splitting. The correlation observed between the molecular structure and the sign of the quadrupole splitting demonstrates that the sign should depend on the bond angle (∠O-Fe-O) in iron(III) complexes.

The paramagnetic relaxation effects in Mössbauer spectroscopy have been ascribed to fluctuations of magnetic fields arising from flips of electronic spins.[1–3] Such magnetic fluctuations are either a spin-spin or spin-lattice relaxation process. The overall relaxation rate λ_t is expressed as $\lambda_t=\lambda_{SS}+\lambda_{SL}$, where λ_{SS} and λ_{SL} are relaxation rates *via* spin-spin and spin-lattice interactions, respectively. The relaxation time τ_t is the reciprocal of λ_t.

The line shape of the observed Mössbauer spectrum greatly depends on λ_t (or τ_t). The paramagnetic relaxation effects have been studied mainly for high-spin iron(III) species.[4–10] This is because there is a very small contribution from λ_{SL} to the relaxation rates which facilitates a discussion of the correlation between the Mössbauer line shape and the molecular structure.

It has been shown that the sign of the electric-field gradient can be determined by examining the asymmetry in a Mössbauer spectra *via* the paramagnetic relaxation processes.[11,12] Bancroft and co-workers[5] claimed that the asymmetric line shapes observed in Mössbauer spectra of a few tris(β-diketonato)iron(III) complexes indicate the presence of positive electric-field gradients. However, the experimental evidence seems to be too ambiguous to support their conclusion. Recently, we studied the paramagnetic relaxation effects in the Mössbauer spectra of eleven tris(β-diketonato)iron(III) complexes using the Mössbauer linewidth as a measure of the relaxation time. We found that the relaxation time increases with an increase in the iron–iron distance but decreases with an increasing temperature.[13] Although the Mössbauer spectra of most complexes were composed of a broad symmetric singlet, asymmetric peaks were observed in several complexes with relatively short relaxation times. Besides, there were complexes which seemed to have negative quadrupole splittings.

In general, it is difficult to definitely prove the presence of small quadrupole splittings. However, it should be possible to determine the sign as well as the presence of a small quadrupole splitting in high-spin iron(III) compounds by examining the change of the Mössbauer line shape associated with the paramagnetic relaxation time.

In the present work, we have measured the Mössbauer spectra of iron(III) complexes diluted in diamagnetic compounds in order to vary the paramagnetic relaxation time due to the spin–spin interaction. The temperature-dependence of the Mössbauer line shape in these systems was also examined because the relaxation time was varied with the temperature through the spin-lattice interaction.

Based on the sign of the quadrupole splitting determined utilizing paramagnetic relaxation effects, we discuss here the molecular structures, especially the coordinating bond angle of tris(β-diketonato)iron(III) complexes.

Experimental

Materials. The iron(III) compounds studied in this work are summarized in Table 1. Most compounds were synthesized and/or purified by modifying some procedures mentioned in the literature.[14–16] The purities of the ob-

Table 1. The elementary analyses of iron(III) chelate compounds

Complexes*	C (%)		H (%)		N or Cl (%)	
	Found	Calcd	Found	Calcd	Found	Calcd
$Fe(acac)_3$	50.80	51.02	6.27	5.95		
$Fe(tfa)_3$	34.91	34.92	2.64	2.34		
$Fe(3\text{-}Meacac)_3$	53.20	54.70	6.92	6.88		
$Fe(3\text{-}NO_2acac)_3$	37.33	36.91	3.99	3.72	8.38	8.61
$Fe(3\text{-}Clacac)_3$	38.63	39.47	4.00	3.97	23.85	23.30
$Fe(3\text{-}Phacac)_3$	66.52	68.17	5.70	5.72		
$Fe(trop)_3$	59.26	60.17	3.76	3.61		
$Fe(oxin)_3$	65.71	66.42	3.73	3.69	8.59	8.61

* acac: $CH_3COCHCOCH_3^-$, tfa: $CF_3COCHCOCH_3^-$, 3-Meacac: $CH_3COC(CH_3)COCH_3^-$, 3-NO$_2$acac: $CH_3COC(NO_2)COCH_3^-$, 3-Clacac: $CH_3COCClCOCH_3^-$, 3-Phacac: $CH_3COC(C_6H_5)COCH_3^-$, trop: $C_7H_5O_2^-$, oxin: $C_9H_6NO^-$.

tained compounds were checked by elementary analysis, and UV-visible and infrared spectroscopy. The results of the elementary analyses are summarized in Table 1.

Solid solutions of (Fe, Al)(oxin)$_3$ were prepared by coprecipitating oxinates of iron(III) and aluminum(III). After an 8-quinolinol (oxine) ethanol solution was added (slightly in excess) to an aqueous solution of $FeCl_3$ and $AlCl_3$ with known concentrations, the pH in the mixed solution was quickly adjusted to about 7 with a sodium acetate aqueous solution. The mole fraction of Fe(oxin)$_3$ in the precipitate was determined by means of colorimetry. Solvated compounds, Fe(acac)$_3$·2CHCl$_3$ and Fe(acac)$_3$·2CH$_2$Cl$_2$, were prepared by recrystallizing from each solvent[17] and their compositions were checked by measuring the weight-loss during storage in air after a Mössbauer measurement.

Measurements of Mössbauer Spectra. Mössbauer spectra were recorded at 78, 195, and 295 K using a Shimadzu MEG-2 or an Austin S-600 Mössbauer spectrometer. An iron foil was used for the calibration of Doppler velocity.

Results and Discussion

Determination of Sign of Quadrupole Splitting from Change in Mössbauer Line Shape. *(a) Solid Solution*: Figure 1 shows the Mössbauer spectra at 78 K of neat Fe(oxin)$_3$ and solid solutions of (Fe,Al)(oxin)$_3$. The line shape may be regarded as a symmetric doublet in the neat Fe(oxin)$_3$. The right (higher energy side) component of the doublet tends to collapse and broaden as the Fe(oxin)$_3$ content in solid solutions decreases, leading to larger distance between Fe(oxin)$_3$ molecules and thus to longer relaxaton time. The two peaks eventually merge into an asymetric single peak.[18] Since the electric-field gradient and the quadrupole splitting have the same sign in ^{57}Fe-Mössbauer spectroscopy, it is expected that the right side peak broadens first in the presence of positive quadrupole splitting whereas the left side peak collapses first in case of negative quadrupole splitting.[19] Accordingly, the change in the Mössbauer line shape shown in Fig. 1 reveals that the iron in Fe(oxin)$_3$ experiences a positive electric-field gradient and, hence, the sign of the quadrupole splitting is positive. Thus, it is shown that the sign of the quadrupole splitting in high-spin iron(III) compounds can be determined by examining the change in the Mössbauer line shape with a relatively small change in the relaxation time caused by the reduced spin-spin interaction due to the increased distance between Fe(oxin)$_3$ molecules in the (Fe, Al)(oxin)$_3$ system.

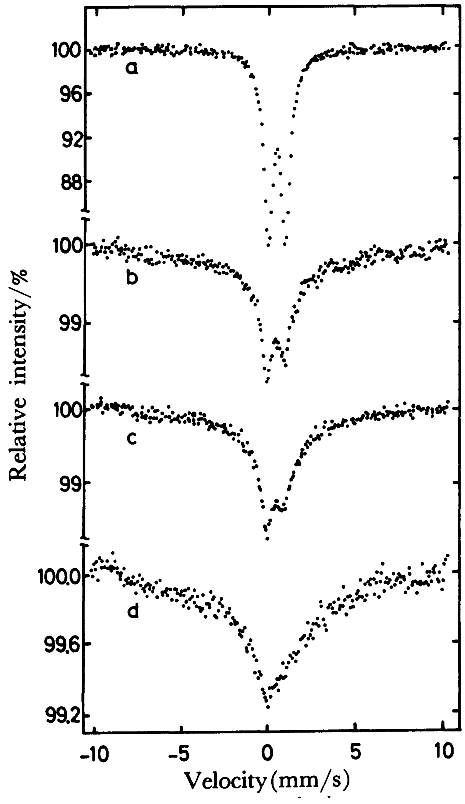

Fig. 1. Mössbauer spectra at 78 K of (Fe,Al) (oxin)$_3$ solid solutions with the Fe(oxin)$_3$ mole fraction of a) 1.0, b) 0.5, c) 0.4, and d) 0.3.

(b) Solvated Compound: Similar experiments were carried out to determine the sign of the quadrupole splitting in Fe(acac)$_3$. However, it proved quite difficult to determine the sign in the systems of (Fe,Al)(acac)$_3$ and (Fe, Co)(acac)$_3$ with this method because of the very small quadrupole splitting expected in Fe(acac)$_3$ and the difficulty in preparing solid solutions with slightly different Fe(acac)$_3$ contents. Accordingly, two solvated compounds, Fe(acac)$_3$·2CHCl$_3$ and Fe(acac)$_3$·2CH$_2$Cl$_2$, were prepared instead to increase the iron–iron distance slightly. The spectra of the solvated compounds at 78 K are shown in Fig. 2 together with neat Fe(acac)$_3$. In Fig. 2, a very small quadrupole splitting is seen in Fe(acac)$_3$ while a sharp singlet peak is observed in each solvated compound. The sharp peak-top position in the solvated compounds agrees exactly with that of the left-component peak in Fe-

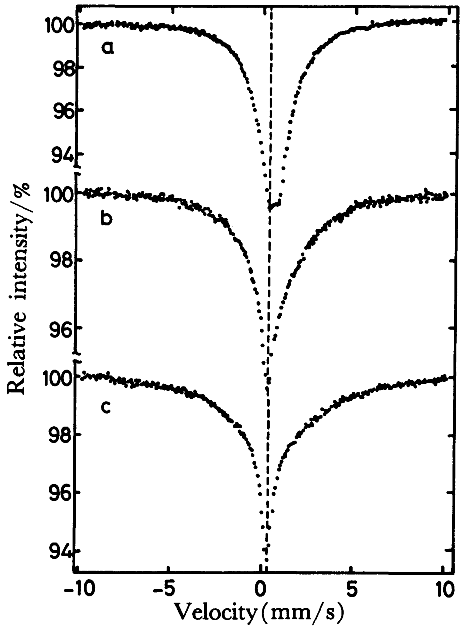

Fig. 2. Mössbauer spectra at 78 K of Fe(acac)$_3$ and its solvated compounds: a) Fe(acac)$_3$, b) Fe(acac)$_3$·2CHCl$_3$, and c) Fe(acac)$_3$·2CH$_2$Cl$_2$.

(acac)$_3$, indicated by the broken line. Furthermore, a slight asymmetry is observed in the line shape of the solvated compounds with a (probably) longer iron–iron distance than in Fe(acac)$_3$. Therefore, it is likely that the sign of the quadrupole splitting in Fe(acac)$_3$ is also positive.

(c) Temperature-dependence: The sign of the quadrupole splitting was determined for five kinds of tris(β-diketonato)iron(III) complexes and Fe(trop)$_3$[20] by examining the temperature-dependence of the Mössbauer line shape. For example, the Mössbauer spectra at 78, 195 and 295 K of Fe(tfa)$_3$ and Fe(3-NO$_2$acac)$_3$ are illustrated in Figs. 3 and 4, respectively.

It is seen in Fig. 3 that the absorption peak of Fe(tfa)$_3$ at 295 K splits in two: at 195 K the right side peak collapses. The spectrum at 78 K apparently has a single peak, although there remains a slight asymmetry. Such a change in the line shape of Fe(tfa)$_3$ with temperature (*i.e.*, relaxation time) may suggest the presence of a positive quadrupole splitting. Since the Mössbauer spectra of Fe(3-Meacac)$_3$ and Fe(trop)$_3$ showed a temperature-dependence similar to that of Fe(tfa)$_3$, their quadrupole splittings should be positive.

In contrast, the left component of the Fe(3-NO$_2$acac)$_3$ peak in Fig. 4 tends to collapse at lower temperatures, indicating the presence of a negative quadrupole splitting. Since the Mössbauer line shapes of Fe(3-Phacac)$_3$ and Fe(3-Clacac)$_3$ showed a temperature-dependence similar to that of Fe(3-NO$_2$acac)$_3$, the sign of their quadrupole splitting may be negative.

Correlation between Sign of Quadrupole Splitting and Molecular Structure. The sign of the quadrupole splitting may be correlated to the molecular structure in accordance with the point-charge model.[21] The quadrupole splitting in high-spin iron(III) compounds is determined by the electric-field gradient produced only by neighboring ions and atoms. The electric field gradient (eq) in tris(β-diketonato)iron(III) can be written as

$$eq = -12\rho \cos\alpha \cdot r^{-3}, \qquad (1)$$

where ρ is the negative charge on an oxygen atom in β-diketonato ligand, r the iron–oxygen bond length, and α the bond angle ∠O–Fe–O (see Appendix). The quadrupole splitting (ΔEq) is given by

$$\Delta Eq = 1/2e^2qQ(1+\eta^2/3)^{1/2}, \qquad (2)$$

where Q denotes the electric quadrupole moment of nucleus ($Q>O$ in ^{57}Fe) and η the asymmetric constant ($\eta=0$ in this case).

By putting equation(1) into equation(2), we obtain

$$\Delta Eq = -6e\rho Q \cos\alpha \cdot r^{-3}, \qquad (3)$$

which implies that the sign of quadrupole splitting depends only on the angle α: the sign should be positive when $\alpha<90°$ and negative when $\alpha>90°$.

Meanwhile, average α values in Fe(acac)$_3$ and Fe(trop)$_3$ determined by X-ray diffractometry are 87.1°[22] and 77.8°[23] respectively. Based on the present model, the sign of a quadrupole splitting should be positive for both compounds, in agreement with the results deduced from the Mössbauer line shape in the present work. Thus, it may be assumed that the bond angle α is also smaller than 90° for Fe(tfa)$_3$ and Fe(3-Meacac)$_3$ whose quadrupole splittings proved to be positive based on the Mössbauer line shape.

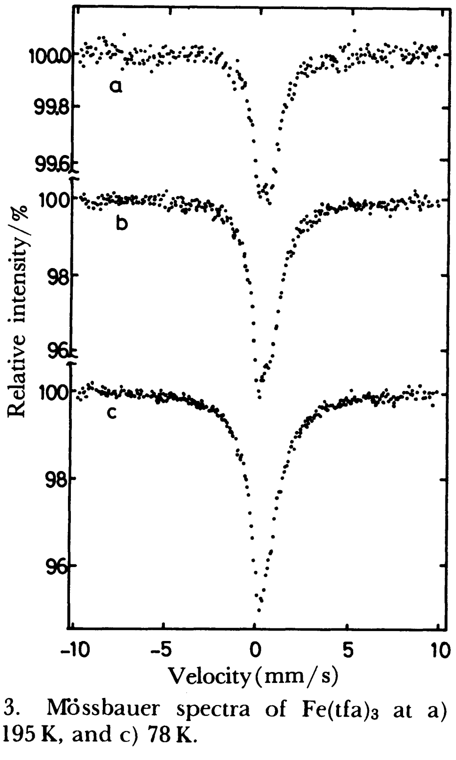

Fig. 3. Mössbauer spectra of Fe(tfa)$_3$ at a) 295 K, b) 195 K, and c) 78 K.

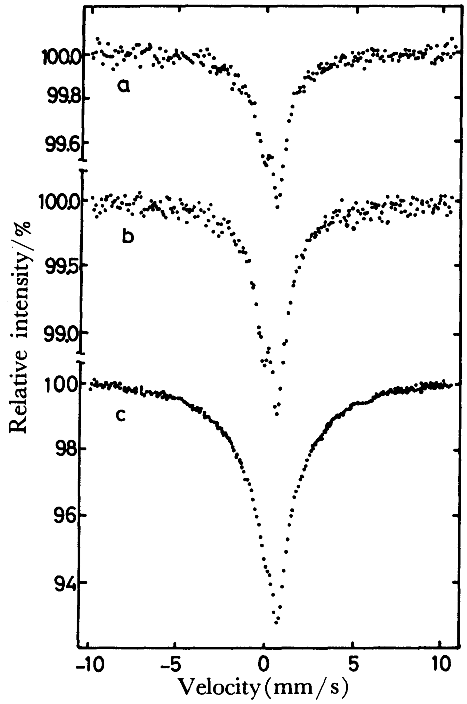

Fig. 4. Mössbauer spectra of Fe(3-NO$_2$acac)$_3$ at a) 295 K, b) 195 K, and c) 78 K.

It appears that α is larger than 90° in compounds complexed with ligand β-diketones containing more bulky 3-substituent groups such as $-NO_2$, $-C_6H_5$, and -Cl, while α is smaller than 90° in the compounds with ligands containing relatively smaller 3-substituent groups, *i.e.*, -H and $-CH_3$. Accordingly, it may be concluded that the bond angle α could be enlarged by the steric hindrance between complex molecules with a bulky 3-substituent group. A further study of these systems will be necessary to validate such a conclusion.

Appendix

If an ^{57}Fe nucleus is located at the origin of the coordinate system (Fig. 5), the electric-field gradient ($V_{zz}=eq$) due to point charges about the nucleus is given by

$$eq = \sum_i \rho_i r_i^{-3}(3\cos^2\theta_i - 1), \tag{4}$$

where ρ_i denotes the i-th point electric charge, θ_i the acute angle between the line segment from the i-th point to the origin and the Z axis (in accordance with the principal axis of electric-field gradient), r_i the distance between the i-th point charge and the origin, and e the protonic charge.

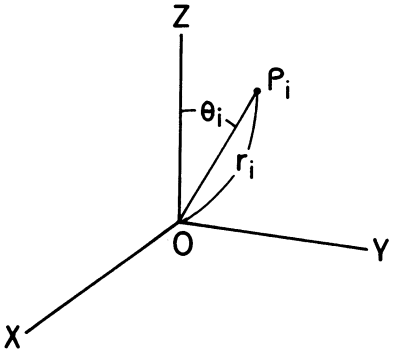

Fig. 5. Coordinates of point charges.

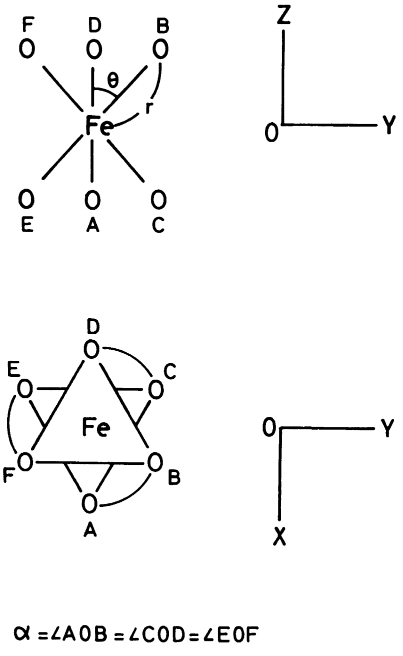

Fig. 6. Arrangement of coordinate atoms in tris(β-diketonato)iron(III) (Iron atom is situated on the origin(0,0,0)).

The Z axis can be determined in tris(β-diketonato)iron(III) complexes as illustrated in Fig. 6. If space coordinate of oxygen atom(A) in a ligand β-diketone is ($r\sin\theta$, 0, $-r\cos\theta$), that of oxygen atom(B) is ($1/2r\sin\theta$, $\sqrt{3}/2r\sin\theta$, $r\cos\theta$). The distance $\overline{AB}$ is given by

$$\overline{AB} = r(1+3\cos^2\theta)^{1/2}.$$

and ∠AOB (*i.e.* ∠O-Fe-O=α) is expressed as follows:

$$\cos\alpha = (1-3\cos^2\theta)/2. \tag{5}$$

Equation(5) also holds for the other two β-diketone ligands. Hence, putting equation(5) into equation(4), we obtain

$$eq = -2\cos\alpha\cdot\sum_i(\rho_i r_i^{-3}).$$

Assuming that each ρ_i or r_i is equivalent in three ligands, we can express the electric-field gradient as

$$eq = -12\rho\cos\alpha\cdot r^{-3}. \tag{6}$$

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18) The Mössbauer spectrum at 78 K of (Fe,Al)(oxin)$_3$ was previously reported at a lower concentration Fe(oxin)$_3$ (3%) than in the present work, showing the line shape with the slower relaxation time reasonably.[24]

19) The magnetic hfs in the ^{57}Fe Mössbauer spectrum corresponds to six transitions ($\pm3/2\rightarrow\pm1/2$, $\pm1/2\rightarrow\pm1/2$ and $\pm1/2\rightarrow\mp1/2$), or combination of three doublets. In the presence of a quadrupole splitting, two lines corresponding

to $\pm 3/2 \rightarrow \pm 1/2$ and $\pm 1/2 \rightarrow \pm 1/2, \mp 1/2$ transitions respectively appear in the spectrum: the right hand (higher energy) component is attributed to the $\pm 3/2 \rightarrow \pm 1/2$ transitions if quadrupole splitting is positive, while the left hand component is attributed to the $\pm 3/2 \rightarrow \pm 1/2$ transitions for negative quadrupole splitting. Furthermore, the doublet due to the $\pm 3/2 \rightarrow \pm 1/2$ transitions has the largest splitting. Hence, there exists a range of magnetic relaxation time in which the $\pm 3/2 \rightarrow \pm 1/2$ line broadens whereas the $\pm 1/2 \rightarrow \pm 1/2, \mp 1/2$ lines are still sharp.[3]

20) Tropolone is not β-diketone, but $\mathrm{Fe(trop)_3}$ is similar to tris(β-diketonato)iron(III) in magnetic properties and molecular structure.

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