Cofacial Metallocene Rings: Evidence for Interaction from Metal Atom Vibrational Anisotropies

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Temperature-dependent Mössbauer spectroscopy has been used to study the details of the metal atom motion in a number of “face-to-face” ferrocenyl moiety containing solids. While the hyperfine parameters for the 1,8-bis(ferrocenyl)naphthalene complexes are very similar to those observed for other ferrocenyl-group-containing organometallics, the “face-to-face” complexes show an unusual Gol’danskii−Karyagin asymmetry, which is not observed for the 1,5-bis(ferrocenyl) homologue. High-temperature data show that the difference in the mean-square-amplitude of vibration parallel and perpendicular to the symmetry axis running through the Fe atom is $\sim 9.3 \times 10^{-19}$ cm^2 at 378 K when the ferrocenyl group is bonded directly to the naphthalene backbone and $\sim 4.6 \times 10^{-19}$ cm^2 when there is an intervening carbon−carbon triple bond. One-electron oxidation of the 1,8-bis(ferrocenyl)-naphthalene complex leads to a cation in which there is no electron exchange between the two iron atoms on the Mössbauer time scale. The oxidized metal atoms evidence spin−lattice relaxation phenomena with very fast relaxation rates above $T \geq \sim 200$ K. The nonoxidized iron atom clearly exhibits anisotropic vibrations at $T \geq \sim 270$ K.

Introduction

Because of their potential use as advanced materials, organometallic arrays,[1] especially those composed of stacked planar units,[2] have received increasing attention in recent years. Within this class of material, polymers constituted of metallocene units have occupied a position of special interest, since the metals are subject to reversible single-electron redox reactions. A number of such stacked oligomeric and polymeric metallocene systems have been reported, based on metallocene units held in a “face-to-face” orientation through their *peri*-substitution on a naphthalene spacer unit.[3] The synthesis, structure, and properties of 1,8-diferrocenylnaphthalene, the model monomer for these systems, was first reported in 1985.[4] The crystal structure of the BF_4^- salt of this complex has also been discussed in the literature,[5] as has that of the “face-to-face” stack of the $n = 2$ oligomer of 1,8-bis(ferrocenyl)naphthalene.[6]

Despite the earlier crystallographic description of these complexes, the question of the direct interaction of the ferrocenyl groups in such face-to-face complexes, and its relationship to the detailed molecular level architecture, is a still incompletely understood phenomenon. It is in this context that temperature-dependent Mössbauer effect spectroscopy can serve to elucidate the details of the metal atom motion in these complexes and provide information concerning the anisotropy of this motion under various geometrical constraints. As will be discussed below, this motional anisotropy is directly related to the question of ring−ring interaction in these cofacial structures.

As has been amply demonstrated in the recent literature,[7] although the usual hyperfine interactions extracted from ^{57}Fe temperature-dependent Mössbauer spectroscopy, such as the isomer shift (IS) and quadrupole splitting (QS), are relatively insensitive to ring substitution in ferrocene-related solids, both the recoil-free fraction related to the spectral area (*A*) and the motional anisotropy of the metal atom as evidenced in the asymmetric spectral shape can be related to both intra- and intermolecular interactions in metallocenes. In particular, the vibrational anisotropy with respect

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Table 1. Summary of Mössbauer Data

	1	2	4	3	5[a]
IS(90), mm s^{-1}	0.535(6)	0.599(1)	0.529(1)	0.556(1)	0.502(1)
QS(90), mm s^{-1}	2.410(1)	2.327(7)	2.406(1)	2.354(2)	2.348(9)
$-$dIS/dT, mm s^{-1} K^{-1} × 10^{-4}	5.31(10)	5.35(13)[b]	5.60(5)[c]	5.16(10)[d]	4.09(14)
$-$dQS/dT, mm s^{-1} K^{-1} × 10^{-4}	8.31(54)		8.03(57)	7.74(65)	
$-$d ln A/dT, K^{-1} x 10^{-3}	8.69(29)	6.28(22)[e]	4.88(10)	8.37(16)	8.93(44)
M_{eff}[f], Da	78	80	74	81	
Θ_M, K	107	125	146	107	
N/κ^2 (90 K), cm^2 × 10^{-19}	0	0.33	~0	0	
N/κ^2 (300 K), cm^2 × 10^{-19}	5.65	7.49	~0	1.91	
N/κ^2 (378 K), cm^2 × 10^{-19}	9.22	9.39	~0	4.59	

[a] Diamagnetic doublet only. [b] High T slope, $210 < T < 370$ K. [c] High T slope, $297 < T < 383$ K. [d] High T slope, $230 < T < 375$ K. [e] High T slope, $250 < T < 370$ K. [f] From high T slopes.

to the highest symmetry axis in the molecule can provide a descriptive parameter associated with the environment around the metal atom. The effect on Mössbauer spectra of the temperature-dependent vibrational anisotropy is generally referred to as the Gol'danskii–Karyagin effect (GKE)[8] and has been reported[9] for a number of organotin complexes, making use of the 23.4 keV γ-radiation from ^{119}Sn. The demonstration of the GKE in organo-iron complexes has been much more limited. Nakashima et al.[10] have reported the enclathration of several halo-ferrocenes in deoxycholic acid, leading to anisotropic motion, while Trautwein et al.[11] have studied a similar effect in barium and guanadinium $Fe[(CN)_5NO]\cdot 3H_2O$), but in these cases the anisotropy is related to the motion of the haloferrocene or nitroprusside group as a whole, respectively, rather than that of the metal atom by itself. True atomic anisotropy evidencing small temperature-dependent intensity effects has been reported[12] for *cis*- and *trans*-$[FeCp(CO)_2]_2$. In a recent series of studies,[13] it has been shown that metal atom vibrational anisotropy in ferrocene and ferrocene-related materials is much more common than was originally thought, although these effects are, generally, quite small.

In the present study, the hyperfine interactions, recoil-free fraction, and vibrational anisotropy of the iron atom have been determined for a number of structurally related cofacial ferrocenes and related complexes, specifically 1,8-bis(ferrocenyl)naphthalene (**1**) and its tetrafluoroborate salt (**5**), 1,1′-bis(8-ferrocenyl-1-naphthyl)ferrocene (**2**), 1,8-bis(ethynylferrocene)naphthalene (**3**), and 1,5-bis(ferrocenyl)naphthalene (**4**), and these parameters have been related to the molecular level architecture of these solids.[5,6]

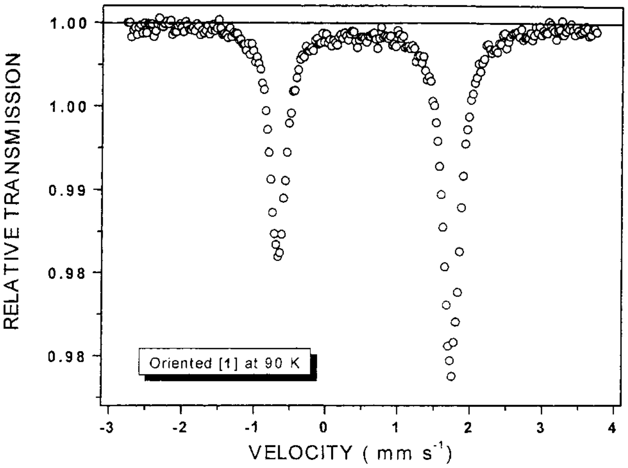

Figure 1. Mössbauer spectrum of oriented crystals of **1** at 90 K.

Results and Discussion

With the exception of **5**, the Mössbauer spectra of all of the neutral complexes consist of well-resolved doublets, and the 90 K values for the IS, QS, ln(A), and their temperature dependencies are summarized in Table 1. The IS(90) and QS(90) values are quite similar to those reported for other ferrocene-related complexes and are otherwise unremarkable. The temperature dependencies of these parameters will be considered in greater detail, below.

The crystal structure of compound **1** has been reported in detail by Rosenblum et al.[4] and shows that this solid consists of loosely packed molecules with no intermolecular contacts less than 3.47 Å. The structure was refined with anisotropic temperature factors for Fe, and $R_w = 0.045$ for 2157 reflections. It can be seen from Figure 1 of this reference that there is significant anisotropy in the iron atom motion at 21.1 °C. Before discussing the spectroscopic results obtained using an absorber in which the microcrystallites are randomly oriented, it is appropriate to report the following observations. The Mössbauer spectra of an absorber in which the crystals have been arranged so that the long needle axes are perpendicular to the γ-ray axis show a very large intensity asymmetry (R) which is temperature-independent. A typical spectrum of such an absorber is shown in Figure 1. At 90 K, this asymmetry, R, $[=A(+)/A(-)]$ is 1.55 ± 0.02. The greater intensity of the component at positive velocity with respect to the spectrum centroid is consistent with $V_{zz} < 0$; that is, the electric field gradient is negative. This is consistent with the classic 1964 study by Collins[14] of the parent

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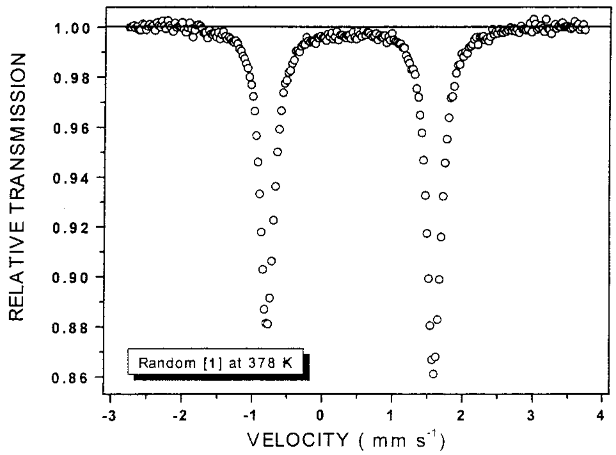

Figure 2. Mössbauer spectrum of randomly oriented microcrystallites of **1** at 378 K.

ferrocene and has been observed in other ferrocene complexes.

In contrast, an absorber with randomly dispersed microcrystallites, obtained by grinding the neat solid with quartz glass powder and dispersing this in BN, shows an R value of 0.97 ± 0.01 at 90 K, but this parameter is temperature-dependent, as will be discussed below. It should be noted that even with this randomization there is a small temperature-independent residual orientation effect observable in the spectra. This "texture" effect has been corrected for in the following discussion. The two components of the resonance spectrum have full widths at half-maximum of 0.271(1) and 0.270(1) and 0.244(2) and 0.243(2) mm s^{-1} at 90 and 378 K, respectively. The larger line width at the lower temperature is presumably due to saturation effects. The temperature dependence of the IS shows the usual curvature at low (90−200 K) temperatures, but becomes linear above this range with a slope of $-(5.32 \pm 0.10) \times 10^{-4}$ mm s^{-1} K^{-1} (cc 0.998 for 12 data points). The effective vibrating mass (M_{eff}) calculated[15] from this value is 78.3 Da, significantly higher than the "bare atom" mass of 57 Da, reflecting the covalency of the metal−ligand interaction. It is, however, noteworthy that this value is noticeably smaller than M_{eff} reported[16] for ferrocene itself, suggesting a qualitatively different interaction between the metal atom and its nearest neighbor environment. The ln(A) temperature dependence similarly shows curvature at low temperatures, but again reaches a linear dependence above 200 K, with a slope of $-(8.67 \pm 0.30) \times 10^{-3}$ K^{-1} (cc 0.966 for 11 data points). From this and the preceding high-temperature limiting values, the Mössbauer lattice temperature (Θ_M) is calculated to be ~107 K.

As noted above, the R parameter for the random orientation sample at low temperatures is very close to unity, but becomes significantly larger at $T \geq 270$ K. A typical spectrum of **1** at 378 K is shown in Figure 2. The origin of this *temperature-dependent intensity asymmetry* is to be found in the anisotropy of the metal atom motion relative to the local symmetry axis (presumed to be normal to the cyclopentadienyl ring planes) and, as noted above, is referred to as the GKE.[8] The GKE and its relationship to the cofacial Cp ring interactions will be discussed more fully below. It is worth commenting that in the majority of alkyl-substituted and related non-face-to-face ferrocenyl complexes, such as methyl ferrocene, 1,1′-dimethylferrocene, and ferrocene methanol, inter alia, no significant temperature-dependent asymmetry is experimentally observable to within ~0.5 deg of the melting point.

The synthesis and X-ray crystallographic structure of the tri-iron face-to-face oligomer of **1** (**2**) has been described by Foxman, Gronbeck, and Rosenblum.[6] The structure was refined using anisotropic temperature factors for Fe in the final refinement at 21 °C (R_w = 0.0629 for 3316 reflections). These authors note that a salient feature of the oligomer structure is that the significant molecular distortions noted in **1** are preserved in **2**; that is, the splaying of the face-to-face Cp rings and the rotation of these rings from an orientation perpendicular to that of the naphthalene rings is maintained. Qualitatively, the Mössbauer spectroscopic results for **2** are very similar to those summarized for **1**, but it is worthwhile noting that despite the presence of two different types of iron atoms in this structure, the Mössbauer measurements cannot resolve these differences, and thus all of the results cited in the following pertain to an average of the two different metal centers. The IS(90) and QS(90) and their temperature dependencies are summarized in Table 1. The high-temperature-limiting slope of IS(T) leads to M_{eff} = 79.5 Da, and the ln $A(T)$ high-temperature-limiting slope combined with this value leads to $\Theta_M = 125$ K. The temperature-dependent intensity asymmetry data for **2** are quite comparable to those noted for **1**, consistent with the structural details reported for the oligomer of Rosenblum et al., and will be discussed in detail, below.

The synthesis and redox chemistry of 1,8-bis(ferrocenylethynyl)naphthalene (**3**) has been reported by Robinson et al.,[17] and a crystal structure is to be published. Suffice it to say at this point that the two cofacial ring planes are inclined at 80.87(7)° and 76.12(7)° to the naphthalene ring plane, and their ring centroids are 3.575 Å apart. The 90 K values of the IS, QS, and the pertinent temperature dependencies and derived data are summarized in Table 1.

The synthesis and structure of the 1,5-homologue of **1** (**4**) has been reported by Robinson et al.[18] The solid consists of well-separated molecules lying about inversion centers, and all intermolecular contacts are larger than 3.5 Å. The ferrocenyl groups are inclined at angles of 47.0(2)° with respect to the naphthalene planes and the ferrocene moieties are twisted in a fashion similar to that observed in **1**. The hyperfine parameters at 90 K and their temperature dependencies are included in Table 1 and are similar to those observed for **1** and **2** (except for the value of Θ_M), including M_{eff} extracted from the second-order Doppler shift data. What is of particular interest is the absence of any significant

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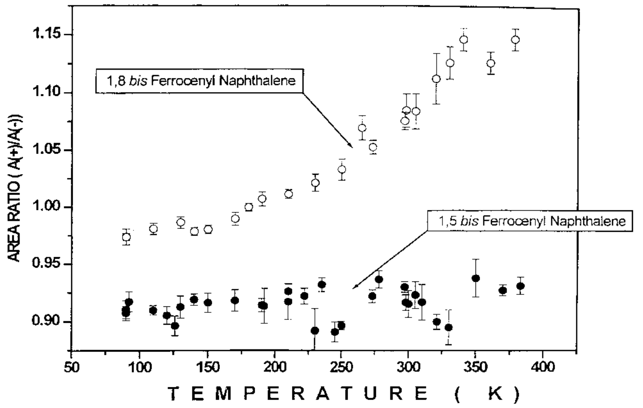

Figure 3. Comparison of the temperature-dependent area ratio for **1** and **4**. The nonunity values in the low-temperature limit reflect a residual orientation (temperature-independent) effect in these samples.

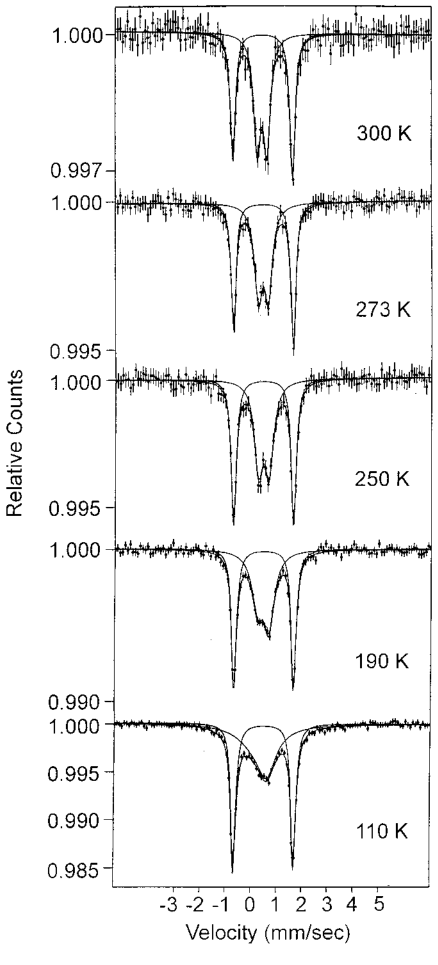

Figure 4. Mössbauer spectra of the one-electron oxidation product of **1** at various temperatures.

temperature-dependent intensity asymmetry as summarized in Figure 3 (lower curve). This absence in **4** and its significance with respect to the question of cofacial interactions of the Cp rings is examined in the following discussion.

Representative ^{57}Fe Mössbauer spectra of the tetrafluoroborate salt **5** at several temperatures are shown in Figure 4 and are seen to be made up of a sharp outer doublet and an inner asymmetric doublet consisting of broad lines, changing in shape with temperature. The Mössbauer spectrum of **5** at 48 K has been previously reported by Rosenblum et al.[3a] The values IS(90) = 0.502 ± 0.006 mm s^{-1} and QS(90) = 2.348 ± 0.006 mm s^{-1} for the outer doublet and the similarity between these values and the parameters for **1** at the same temperature (Table 1) leave little doubt that one of the two iron atoms in the one-electron oxidation product is essentially indistinguishable from that in the neutral homologue. Moreover, the observation of the two-doublet resonance pattern shows clearly that on the Mössbauer time scale there is no charge exchange between the two iron atoms, as noted previously[3a] at 48 K. This absence of charge equalization might have been expected due to the presence of the σ bond tethering the ferrocene (ferrocenium) moieties to the naphthalene backbone.

The inner doublet subspectrum is associated with the iron atoms (50%) which have lost one electron and thus have become magnetic with nonzero spin. The spectra, some of which are shown in Figure 4, have been analyzed in terms of two subspectra of equal intensity (spectral area), one of which is the normal narrow doublet, identical to the doublet observed in the other neutral complexes of this series, and the other exhibiting temperature-dependent slow paramagnetic relaxation behavior. For a negative quadrupole interaction and in the high-temperature spin relaxation limit of a paramagnetic iron ion, the spectrum is expected to consist of two broadened lines, with the lower energy line (corresponding to the $\pm 3/2 \leftrightarrow \pm 1/2$ transition) broadened considerably more than the higher energy line. Raising the temperature should increase the relaxation rate and, thus, narrow the lines to the limit of a natural line width doublet of equal depth. Simple Mössbauer spin relaxation theory[19] has been used to effect a comparison between the least-squares fit of the experimental and theoretical spectra. This fit has been found to be extremely good, and the obtained parameters show that the spin relaxation rate is a steeply increasing function of T, as expected for spin–lattice relaxation.

As noted above, the outer narrow doublet behaves similarly to the spectra observed for **1**, **2**, and **4**. The high-temperature spectra, Figure 4, even show the presence of a GKE phenomenon. At 310 K, the area ratio is 1.18. In this context it is also worth noting that while the outer doublet becomes asymmetric as the temperature is raised (due to the GKE), the inner doublet becomes symmetric due to the fast spin–lattice relaxation.

In crystals in which the mean square vibrational amplitude of the metal atom parallel to the highest symmetry crystal axis ($\langle x^2_{\mathrm{para}}\rangle$) is different from that perpendicular to this axis ($\langle x^2_{\mathrm{perp}}\rangle$), the Mössbauer recoil-free fraction f is anisotropic and leads to a temperature-dependent nonequal intensity of the two line patterns of quadrupole-split ^{57}Fe and ^{119}Sn Mössbauer spectra in powder samples, i.e., the Gol'danskii–Karyagin effect.[20] The ratio R of the intensities of the $\pm 3/2 \leftrightarrow \pm {}^{1}/_{2}$

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line (π), which has pure $\Delta m = \pm 1$ character, to that of the $\pm 1/2 \leftrightarrow \pm 1/2$ line (σ), which has a mixture of both $\Delta m = 0$ and $\Delta m = \pm 1$ character, depends on temperature through a single parameter, N, given by

$$N = \kappa^2(\langle x^2{}_{\mathrm{para}}\rangle - \langle x^2{}_{\mathrm{perp}}\rangle)$$

where κ is the Mössbauer γ-ray wavenumber.[20]

Numerical plots of $R(N)$ are readily obtained from the literature (see Figure 1.33 of ref 20). Thus, for a randomly oriented powder sample, the experimental determination of $f_{\mathrm{av}}(T)$ and $R(T)$, which yields directly $N(T)$, determines $\langle x^2{}_{\mathrm{para}}\rangle_T$ and $\langle x^2{}_{\mathrm{perp}}\rangle_T$ for the resonantly absorbing atom in the structure. The average recoil-free fraction, f, can be obtained from the spectral area of the sample compound at a given temperature, and the spectral area of a reference compound which, in the present case, is metallic (α) iron foil.

The temperature dependence of $\langle x^2{}_{\mathrm{para}}\rangle_T$ and $\langle x^2{}_{\mathrm{perp}}\rangle_T$ can be characterized by a single parameter using the Debye model of solids. The value of $\langle x^2\rangle$ is given in this case by

$$\kappa^2\langle x^2\rangle = (6R_c/k_B\Theta_D)[1/4 + (T/\Theta_D)^2 \int_0^{\Theta/T} x\,\mathrm{d}x/(\mathrm{e}^x - 1)]$$

in which $R_c = \{(h/2\pi)\kappa\}^2/2M$ is the recoil energy of the absorbing atom or cluster of mass M.

In predominantly ionic iron complexes, it is assumed that $M = 57$ Da. However, in covalent solids, a more realistic value of this mass, M_{eff}, can be obtained[15] from the temperature dependence of the isomer shift (in the high-temperature limit). Such values of M_{eff} (also listed in Table 1) are generally significantly larger than 57 Da, due to covalency effects, and thus lower values of Θ_D are obtained, as summarized in Table 1. In the following discussion, the experimentally determined value $M_{\mathrm{eff}} = 79 \pm 2$ Da has been used in the lattice temperature calculations.

With respect to the ferrocenyl complexes of the present study, it should be noted immediately that compounds **1**, **2**, and **3** evidence very significant Gol'danskii−Karyagin asymmetry, while the 1,5 complex (**4**) is similar to other non-face-to-face ferrocenyl complexes in that it *shows no temperature-dependent intensity asymmetry over the range* $90 < T < 370$ *K* (see Figure 3), suggesting immediately the relationship between the GKE and molecular structure. In this context it is worth noting—as Simpson et al.[17,18] observe—that the Fc groups are inclined at angles of 47.0(2)° with respect to the naphthalene mean plane, and the twisting of these Fc moieties in **4** is similar to those observed [45.0(1)° and 47.0(1)°] for the more sterically crowded **1**. The severe distortions of the naphthalene fragment observed in **1** are not evident in **4**. The displacement of the Cp ring which is carbon bonded to the naphthalene fragment is only 0.021(9) Å, compared to values in excess of 0.07 Å in the 1,8 complex.

Turning now to a consideration of the individual complexes, a typical plot of R versus T for **1** and **4** is summarized in Figure 3. It is seen from this figure that for both compounds R is essentially temperature invariant below ~150 K, but for **1** rises significantly with increasing temperature above this value, while it remains T-independent for **4**. Making use of the calculated recoil-free fraction for **1** at $T = 298$ K (as described above) and the experimental values of the area under the resonance curve [$A(T)$] and the area ratio [$R(T)$], the mean-square amplitudes of vibration parallel and perpendicular to the molecular symmetry axis can be calculated. These data can then be fitted to assumed Mössbauer lattice temperatures (Θ_M) as shown in Figure 5. From these data it is clear that the Debye model is not a very good approximation for the present system, in particular at low temperatures. Nevertheless, in the high-temperature limit (linear region) Θ_M can be reasonably well approximated for **1** by $\Theta_{M,\mathrm{para}} = 90$ K and $\Theta_{M,\mathrm{perp}} = 120$ K, where the subscripts refer to motion parallel and perpendicular to the major molecular symmetry axis perpendicular to the two Cp rings. This leads to a "mean" value of $\Theta_M = 110$ K, in good agreement with the value calculated directly from ln $A(T)$ in the high-temperature limit of 107 K. The value of N/k^2 (eq 4) is ~0, 5.7×10^{-19}, and 9.2×10^{-19} cm² at 90, 298, and 378 K, respectively. These data are included in the values summarized in Table 1. Not unexpectedly, the mean-square-amplitude of vibration parallel to the molecular symmetry axis is significantly larger than that perpendicular to this axis, and *this vibrational asymmetry is assumed to arise from the restricted vibrational constraints of the "face-to-face" cyclopentadienyl rings.*

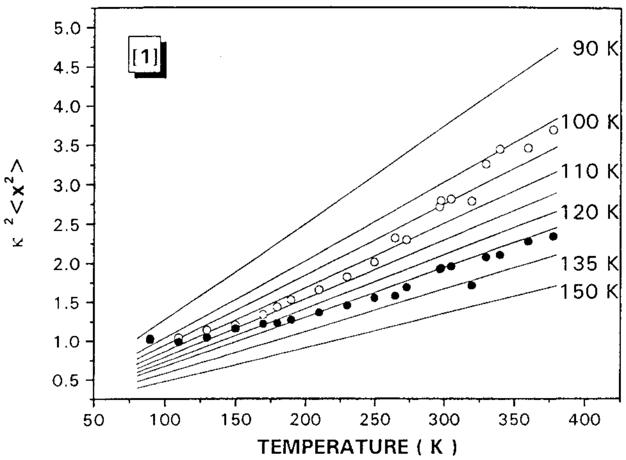

Figure 5. Comparison of the temperature-dependent mean-square-amplitude of vibration parallel and perpendicular to the molecular symmetry axis and the orthogonal lattice temperatures calculated from a modified Debye model.

Analogous results for **2** are also summarized in Table 1. Here, the two values of $\Theta_{M,\mathrm{para}} = 115$ K and $\Theta_{M,\mathrm{perp}} = 145$ K lead to a mean value of $\Theta_M = 135$ K, in reasonable agreement with the value calculated from IS(T) and ln $A(T)$. The values of N/k^2 at three temperatures are also included in Table 1. Finally, in this context, it is worth noting that the differences in mean-square-amplitudes of vibration at the three temperatures are quite similar for **1** and **2**, as is expected from the reported molecular structures.

Turning next to **3**, the two values of $\Theta_{M,\mathrm{para}}$ and $\Theta_{M,\mathrm{perp}}$ are 100 and 110 K, respectively (again, being aware that these parameters are somewhat temperature-dependent), leading to a "mean" lattice temperature of ~107 K, in good agreement with the value of ~107 K calculated from the respective IS(T) and ln $A(T)$ values.

More significant is the fact that the differences in mean-square-amplitudes of vibration in the two directions, while not insignificant, are smaller by more than a factor of 2 (at the same temperature) than was observed for **1** and **2**. This observation is consistent with the somewhat greater flexibility of the face-to-face Cp rings separated from the naphthalene anchor by the two ethyne groups, as compared to the Cp rings directly bonded to the aromatic backbone.

Despite the persuasive evidence for anisotropic metal atom motion in **1** detailed above, a persistent reviewer of this paper has insisted that an experiment of the type suggested by Grenet and Varret[21] be carried out. The purpose of such an experiment is to minimize any possible “texture” effect by orienting the sample holder at the “magic angle” (54.7°) with respect to the normal of the sample plane (35.3° from the radiation axis). Such experiments have subsequently been carried out at 296, 335, and 375 K. The average difference in R [$=A(+)/A(-)$] between the 90° oriented sample and the “magic angle” oriented sample at the three temperatures is 0.021 ± 0.024 and does not show a decrease with increasing temperature if this difference were indeed due to a “texture” contribution. This “null” result clearly shows that the “texture” effect in the nominally randomly oriented sample is, in fact, less than a few percent of the observed intensity asymmetry. Thus, the anisotropy of the iron atom motion in **1** has again been convincingly demonstrated.

In summary, then, the present study has shown that when two ferrocenyl (Fc) moieties are tethered to a (semi) rigid backbone, so that the motional freedom of the Cp rings is significantly inhibited, the metal atom motion becomes strongly anisotropic. This metal atom anisotropy can be seen as diagnostic of significant steric interaction of the Cp rings. Comparison of the 1,8-bis-Fc naphthalene and 1,5-bis naphthalene complexes illustrates the cooperative interaction of the Cp rings in the former and the absence of such cooperative effects in the latter. Extension of these observations to the face-to-face tri-iron complex **2** and the ethyne-spaced di-iron complex **3** provides a self-consistent model of the Cp interactions in such complexes.

Experimental Section

Compounds. The syntheses of **1**, **2**, and **5** have been described in the literature as noted. A sample of **4** was generously made available to us by Prof. B. Robinson and his research group at the University of Otago, as was a sample of **3**, the crystal structure of which has recently been described.[17]

Mössbauer Spectroscopy. The details of the spectroscopic method have been described earlier.[12,16] Several samples of **1** were prepared as follows: one sample (random orientation) was thoroughly ground with quartz glass powder, mixed with BN, and packed into the usual plastic sample holder. Another sample (oriented) was prepared by placing the needlelike solid into the sample holder, using a micro-manipulator, so that the long needle axis was oriented perpendicular to the γ-ray axis. A third sample (for the “magic angle” experiments) was ground with quartz powder, mixed with BN, and packed into an O-ring-sealed sample holder before mounting in the spectrometer, either at 90° or at the “magic angle”. The reasons for using a sealed sample holder, as well as for monitoring the transmission rate before, during, and after data collection, have recently been discussed in detail.[22] Samples of the remaining solids were mounted as random orientation microcrystallites, again using BN as a dispersant.

The Mössbauer source was ~50 mCi ^{57}Co in Rh, and the spectrometer was calibrated using an α-Fe foil at room temperature; all isomer shifts are quoted with respect to the centroid of such spectra. Temperature control was estimated to be constant to better than ±0.2 deg over the time intervals of data accumulation.

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