

Hyperfine Interactions and Metal Atom Dynamic Effects of Pentafluorophenyl Substituents on Ferrocene Complexes

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Received: June 4, 2008; In Final Form: July 7, 2008

Seven ferrocenyl complexes, in which one or more of the Cp ring protons have been substituted by strongly electron-withdrawing pentafluorophenyl groups, have been examined by temperature-dependent ^{57}Fe Mössbauer spectroscopy (MES) to determine both the electronic and dynamic effects of such substitution. The mean-square-vibrational-amplitudes of the metal atom have been expressed in terms of the dimensionless parameter $F_{z,T} = k^2 \langle x_{\text{ave}}^2 \rangle$, where $z=M$ for the Mössbauer data, $z=X$ for the X-ray data, k is the wave vector of the gamma radiation, and $\langle x_{\text{ave}}^2 \rangle$ is the mean square amplitude of the metal atom vibration. The differences between the M and X values can be related to the effects of local (atomic) and non-local (molecular) contributions to the metal atom dynamics. The MES data also elucidate the vibrational anisotropy of the metal atom motion, which in all of the complexes examined is isotropic within the experimental error.

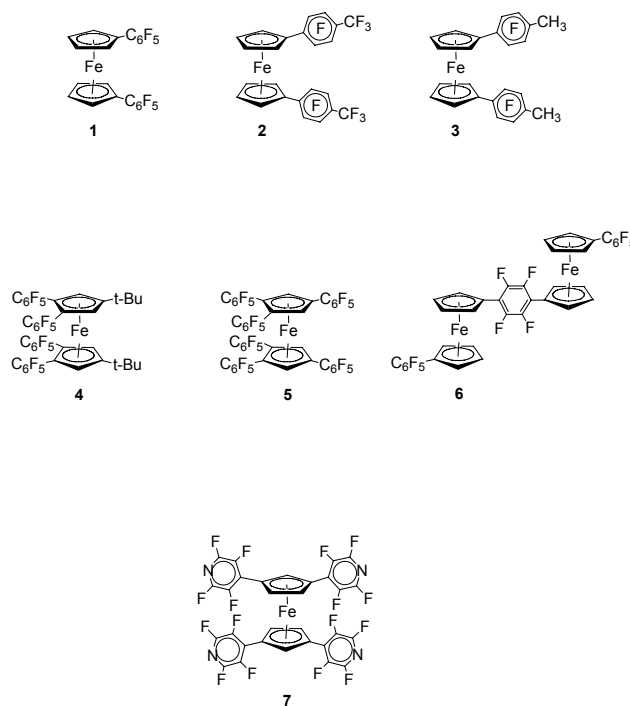
1. Introduction

The recent development of imaginative new synthetic techniques for the preparation of ferrocenes, in which one or more of the Cp ring protons has been replaced by electron-withdrawing per-fluoro substituents,¹ has made it possible to investigate in detail the effects on both the s -electron density at the iron nucleus as well as the dynamics of the metal atom of this substitution. In addition, temperature-dependent Mössbauer effect spectroscopy (MES) has facilitated the comparison of the dynamical behavior of the iron atom in such complexes as extracted from single crystal X-ray diffraction data and that derived from MES measurements and thus to effect a greater understanding of the differences between the local (atomic) and non-local (molecular) motions in such systems.

In the present study, a number of compounds have been examined, including $\text{C}_{22}\text{H}_8\text{F}_{10}\text{Fe}$,² (1); $\text{C}_{24}\text{H}_8\text{F}_{14}\text{Fe}$,³ (2); $\text{C}_{24}\text{H}_{14}\text{F}_8\text{Fe}$, (3); $\text{C}_{42}\text{H}_{22}\text{F}_{20}\text{Fe} \cdot \text{CHCl}_3$,⁴ (4); $\text{C}_{46}\text{H}_4\text{F}_{30}\text{Fe} \cdot \text{C}_6\text{H}_6$,⁵ (5); $\text{C}_{38}\text{H}_{16}\text{F}_{14}\text{Fe}_2$,⁶ (6); and $\text{C}_{30}\text{H}_6\text{F}_{16}\text{FeN}_4$,⁷ (7). For enhanced clarity, the structures of these compounds are collected in scheme 1. In the present study, these compounds have been investigated by temperature-dependent MES and the dynamical data concerning the iron atom(s) have been compared to the temperature factor U_{ij} values determined by single crystal X-ray diffraction. A comparison between the MES and X-ray based data relating to the vibrational amplitudes of the metal atom in organometallics should consider the effect of lattice imperfections which play a more significant role in the magnitude of the U_{ij} values extracted from X-ray diffraction data than in the mean-square-amplitude-of-vibration data contributing to the recoil-free fraction (MES) values. *Inter*-molecular motions will contribute more to the former than the latter, since the X-ray measurements sample all atomic positions over a lengthy period of time while the MES measurements involve only a single atom during the scattering event. It should also be noted that the presence of solvate molecules in the unit cell will influence the atomic positions sensed by the X-ray technique relative to the MES measurements. This point will be addressed again in the discussion to follow. Hence, in general

the vibrational amplitudes calculated from the X-ray data are larger than those derived from the MES data at the same temperature, as will be discussed in greater detail, below. This observation has also been examined in detail in relation to protein dynamics by Parak et al.⁸

The second point relates to the temperature dependence of the vibrational amplitudes. The frequency of such vibrations can be expressed as $\omega \propto [k/M]^{1/2}$ where k is the appropriate force constant and M is the vibrating mass. For *intra*-molecular motions, k is large and M is small (relatively), whereas for *inter*-molecular motions, k is small and M is large. Thus, at low temperatures where the phonon frequencies are low, the major contribution to the vibrational amplitude will be due to the *inter*-molecular motions, while with increasing temperature the *intra*-molecular motions become more appreciable. These considerations lead to the expectation that the tempera-



scheme 1

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ture dependence of the vibrational amplitudes (recoil-free fraction) will depart increasingly from a linear function as the temperature is increased as has been discussed in detail by Gol'danskii and Makarov.⁹ This expectation is, in fact, observed in all of the compounds of the present study.

2. Experimental

(a) The compounds examined in the present study have been generously made available by Prof. P. Deck and his research group who have also described the synthetic techniques involved, as well as the details of the X-ray diffraction results. These samples, which are air stable powders at room temperature, were used as received.

(b) Mössbauer effect spectroscopy. The experimental procedures involved in the MES studies have been detailed previously¹⁰ and were carried out on neat powdered samples held in Perspex sample holders and examined in transmission geometry. Spectrometer calibration was effected using an α -Fe absorber at room temperature, and all isomer shifts are here reported with respect to the centroid of such calibration spectra acquired both before and after the sample runs. The MES spectra consisted in all cases (except where noted) of well resolved doublets, indicating a single iron crystallographic site, and a typical spectrum is shown in Figure 1. Typical line widths (FWHM) of the MES absorption lines in the absence of saturation effects are 0.22–0.25 mm s⁻¹, compared to the theoretical value of 0.194 mm s⁻¹, indicative of single iron site

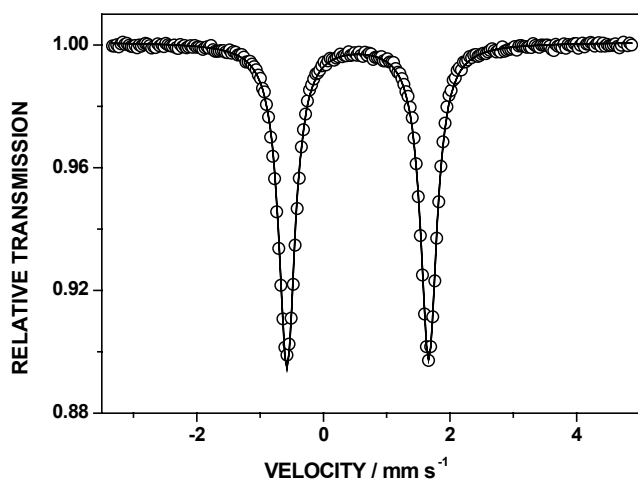


Figure 1. ⁵⁷Fe Mössbauer Spectrum of compound **6** at 89.4 K. The line width (FWHM) is 0.313±0.002 mm s⁻¹ despite the presence of two iron atoms per molecular unit, showing the high crystallographic similarity of the two metal sites.

absorptions in these solids.

3. Results and discussion

Compound 1: Because of the very limited amount of sample available for study, the temperature range appropriate to **1** is severely limited. The resonance effect magnitude at 90 K was only 0.86%, necessitating long data collection times at the higher temperatures. The hyperfine interaction parameters, that is, the isomer shift (IS) and quadrupole splitting (QS) at 90 K, as well as the derived parameters are summarized in Table 1. Ring proton substitution by strongly electronegative groups such as C₆F₅ has only a minor effect on the s-electron density at the metal center, and the replacement of two Cp ring protons by C₆F₅ changes the IS from that observed in the parent ferrocene by only ~0.01 mm s⁻¹ indicating that the iron d-orbitals do not sense the electron withdrawing power of the electronegative groups. The temperature-dependence of the IS is reasonably well fitted by a linear regression (correlation coefficient 0.934 for 7 data points) and leads to a calculated effective vibrational mass,¹¹ M_{eff} , of 140±4 daltons (Da). As noted previously, the difference between this value and the 57 Da associated with a "bare" iron atom reflect the covalency of the metal atom-ligand bonding. The area ratio, $\{R = [A(+)/A(-)]$, where $A(+)$ and $A(-)$ are the areas under the resonance curve of the doublet component at more positive and more negative velocities than the spectrum centroid, respectively}, is temperature independent (0.97±0.03) over the entire temperature range, from which it is inferred that the iron atom motion is isotropic over the interval 90< T <210 K.

The area under the resonance curve, A , for an optically "thin" absorber scales with the recoil-free fraction, f , and hence correlates with the mean-square-amplitude-of-vibration, $\langle x_{\text{ave}}^2 \rangle$, through the relationship $\ln A \propto \ln f = \exp(-k^2 \langle x_{\text{ave}}^2 \rangle)$, where k is the wave vector of the ⁵⁷Fe Mössbauer line. In the present summary, $k^2 \langle x_{\text{ave}}^2 \rangle$ is represented by the symbol F , and for **1** this parameter is a linear function of T . Making the assumption that in the high temperature regime, namely above 0.5 Θ_M , F is a linear function of T and extrapolates to zero as $T \rightarrow 0$, makes it possible to calculate F at all temperatures in the stipulated range. The value calculated from the MES data at 173 K is $F_{M,173} = 1.39(9)$. The F parameter can also be calculated from the $U_{i,j}$ values at 173 K reported in the crystallographic study by Hughes et al.¹² This value is $F_{X,173} = 1.51(4)$, and the difference in the two values can be ascribed to the influence of the static distribution of iron atom positions due to lattice imperfections to which the X-ray data are sensitive, but the MES data are not. In the present case, the small difference in the two values implies that the static lattice distortions are negligibly small in the indicated temperature range. The $F_{M,100}$ value is calculated to be 0.75±0.05.

Compound 2: The hyperfine parameters at 90 K are

TABLE 1: ⁵⁷Fe Mössbauer parameters and derived quantities discussed in the text

Compd.	1	2	3	4	5	6	7
IS(90) /mm s ⁻¹	0.546(7)	0.513(3)	0.533(3)	0.622(4)	0.581(4)	0.544(3)	0.543(4)
QS(90) /mm s ⁻¹	2.290(5)	2.253(3)	2.286(3)	2.491(4)	2.326(4)	2.240(3)	2.137(4)
-dIS/dT /10 ⁻⁴ mm s ⁻¹ K ⁻¹	2.97(28)	3.78(8)	5.00(23)	4.66(17)	7.47(17)	4.84(3)	3.39(9)
-d(ln A)/dT /10 ⁻³ K ⁻¹	7.55(50)	6.95(9)	7.96(42)	7.04(9)	7.76(30)	5.85(5)	6.36(8)
R	0.97(3)	1.03(2)	(T depend)	0.94(2)	0.996(17)	0.99(2)	0.996(20)
M_{eff} /Da	140(4)	110(2)	84(4)	89(3)	90(3)	86(1)	123(3)
$F_{z,T}$	$F_{X,173}=1.51(4)$	$F_{X,100}=0.889(51)$		$F_{X,120}=0.928(9)$	$F_{X,100}=1.07(1)$	$F_{X,298}=1.97(2)$	
	$F_{M,173}=1.39(9)$	$F_{M,100}=0.695(12)$		$F_{M,120}=0.845(11)$	$F_{M,100}=0.78(3)$	$F_{M,298}=1.74(2)$	

included in Table 1 and are not otherwise remarkable. Although there is a fair amount of scatter in the data, the high temperature limiting slope of $d(\ln A)/dT$ is $-(6.95 \pm 0.12) \times 10^{-3} \text{ K}^{-1}$ with an r value of 0.998 for 10 data points. The X-ray data at 100 K have been reported by Deck et al.¹³ and the comparison of the MES and X-ray data lead to $F_{X,100} = 0.89(5)$ and $F_{M,100} = 0.70(1)$ in modest agreement with each other. Again, making the assumption that the linear extrapolation leads in the low temperature limit $F_M \rightarrow 0$, the mean square amplitudes of vibration of the iron atom at the same temperature for **1** and **2** are nearly identical (see above), so that replacement of a phenyl ring F by a CF_3 group has essentially no effect on the iron atom dynamics.

Compound 3: Both the IS and $\ln A$ temperature dependencies for this compound are well fitted by linear regressions and lead to a value of $M_{\text{eff}} = 83 \pm 4 \text{ Da}$. The Mössbauer lattice temperature, Θ_M , is $108 \pm 6 \text{ K}$. The area ratio, R , shows a negative temperature dependence over the range $96 < T < 315 \text{ K}$. The hyperfine parameters, included in Table 1, are not otherwise remarkable.

Compound 4: The temperature-dependence of the IS parameter for **4** shows significant curvature in the low temperature region, but the data in the interval $169 < T < 249 \text{ K}$ are reasonably well fitted by a linear regression with $r = 0.996$ for 5 data points. This high temperature slope yields a calculated $M_{\text{eff}} = 89(3) \text{ Da}$. The temperature-dependence of the $\ln A$ data are closely fitted by a linear regression over the whole range ($86.5 < T < 272 \text{ K}$) with $r = 0.999$ for 10 data points. From this slope and the $d(\ln A)/dT$ value, the Mössbauer lattice temperature, Θ_M , is $110(10) \text{ K}$ justifying the "high temperature limit" assumption. Moreover the $d(\ln A)/dT$ data yield $F_{M,120} = 0.848(2)$, whereas $F_{X,120} = 0.928(9)$ based on the X-ray data of Deck et al.¹⁴ The calculated temperature dependencies of the root-mean-square-amplitude-of-vibration (rmsav) of the iron atom in **4**, as well as the comparable data for ferrocene, are summarized graphically in Figure 2. The values extracted directly from the X-ray U_{ij} values are indicated by the half-filled data points. The area ratio parameter, R , for **4** is nearly temperature-independent [mean value $0.94(2)$ over the whole T range] suggesting that anisotropy in the iron atom motion does not make a significant contribution to the metal atom motion.

Compound 5: This compound was examined by both MES and X-ray methods as the *tetrakis* benzene solvate. The IS and QS are included in Table 1, and are otherwise unremarkable except to note that this compound, which has the largest number of electronegative ring substituents (6), evidences no particularly large effect on the s-electron density at the Fe nucleus. The temperature-dependence of the recoil-free fraction data is summarized in Figure 3 from which it is noted that the 11 data points can be separated into two linear correlations, both with exceptionally high r values. Even making use of the high temperature slope [$-(7.76 \pm 0.30) \times 10^{-3} \text{ K}^{-1}$] leads to a value of $F_{M,100} = 0.78(4)$ much smaller than the X-ray value of $F_{X,100} = 1.071(9)$. This large difference may reflect the presence of the four benzene solvate molecules in the unit cell of the solid, and their effect on the X-ray U_{ij} values, as noted above. The area ratio, R , is shown graphically in Figure 4, and is effectively temperature independent over the temperature range $90 < T < 299 \text{ K}$ [mean value $0.996(17)$ for 11 data points] indicating again the isotropic nature of the Fe atom vibrations, in agreement with the X-ray U_{ij} values which are essentially equal for the three principal components of the thermal factor matrix. It should be noted that the "break" in the $\ln f$ data for **5** is not reflected in the R data summarized in Figure 3 nor is a discontinuity noted in the temperature dependencies of the IS and QS parameters accompanying the $\ln f$ data.

Because of the presence of six C_6F_5 groups it was thought desirable to determine the sign of the QS parameter in this

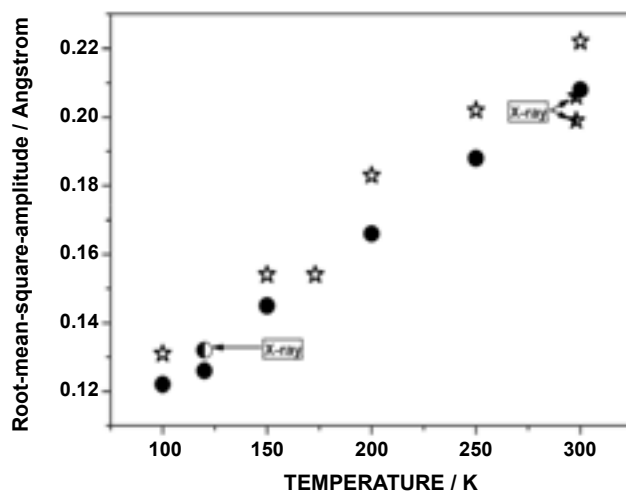


Figure 2. Root-mean-square-amplitudes of vibration as a function of temperature for compound **4** (filled data points) and ferrocene (stars). The half-filled data points are the values calculated from the X-ray U_{ij} data as discussed in the text.

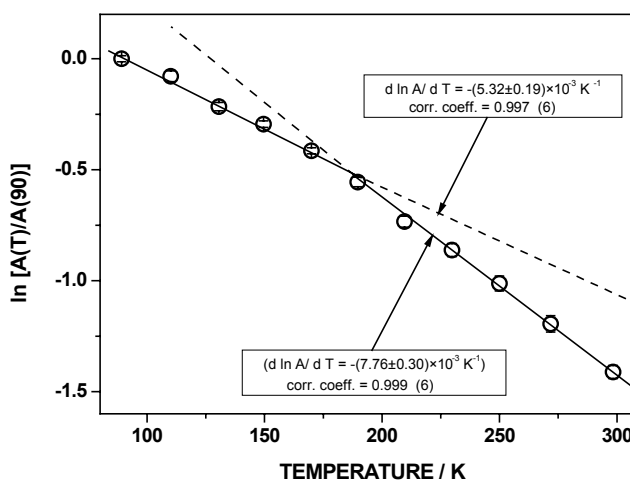


Figure 3. Temperature-dependence of the area under the resonance curve, normalized to the 90 K value, for compound **5**. The value of $F_{M,298}$ reported in Table 1 is taken from the higher temperature regime.

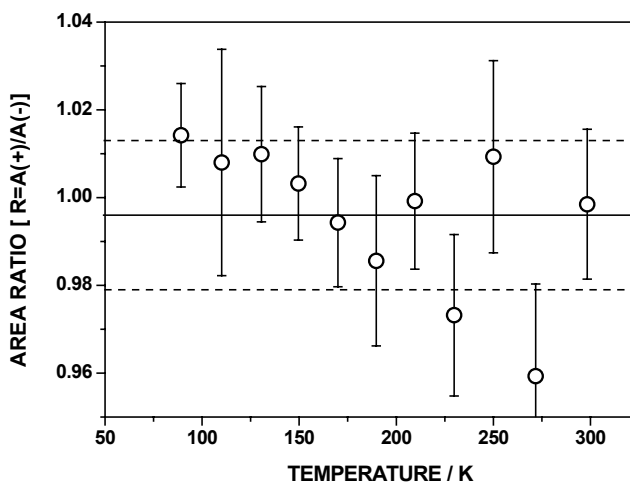


Figure 4. The area ratio R for compound **5** as a function of temperature. The two dashed lines delineate the mean value (solid line) plus/minus one standard deviation and show that over the indicated temperature interval the iron atom motion is essentially isotropic.

compound, using the magnetic field technique, similar to the studies of octamethyl- and decamethyl-ferrocene reported earlier.¹⁵ As in the case of these two ring substituted compounds, as well as for the parent ferrocene, for compound **5** QS is positive at room temperature.

Compound 6: This compound has two C₆F₅ Cp Fe Cp moieties linked by a C₆F₄ fragment and this is expected to be similar in its hyperfine parameter values to those observed for **1** and **2**, and inspection of Table 1 shows that this is indeed the case. Moreover, although there are two iron atoms per molecule, the observed narrow linewidth of the absorption lines, 0.233(2) mm s⁻¹, shows clearly that the metal atoms are in identical environments with respect to the MES parameters. The QS parameter shows the normal negative temperature dependence due to thermal expansion effects. Both the IS and ln A parameters follow a linear temperature dependence. The high temperature limiting slope of ln A, taken to minimize saturation effects, is $-d(\ln A)/dT = (5.85 \pm 0.05) \times 10^{-3} \text{ K}^{-1}$ with $r=0.997$ for 9 data points. This leads to a value of $F_{M,298} = 1.743(15)$ while the X-ray data at 298 K yield $F_{X,298} = 1.974(20)$. The area ratio, R , is essentially temperature independent up to 321 K, again indicating isotropic vibrational motion of the iron atom in the solid.

Compound 7: This compound was studied over the temperature range $90 < T < 294 \text{ K}$ and the lower temperature regime spectra are well fitted by a single doublet, as noted in Table 1. At temperatures above $\sim 130 \text{ K}$ the MES spectra are better fitted by including a small amount of an impurity site, which accounts for up to $\sim 17\%$ of the spectral area at 294 K. The impurity resonance has a QS of $\sim 0.61 \text{ mm s}^{-1}$ compared to $\sim 2.13 \text{ mm s}^{-1}$ for the majority site, but has not been otherwise identified by the presently available data. The presence of this second site has been corrected for in the subsequent data analysis. The T -dependence of the IS of the majority site shows significant curvature over the entire range, so that a reliable value of M_{eff} cannot be calculated. However the $d(\ln A)/dT$ data are well accounted for by a linear regression ($r=0.98$ for 12 data points) and the slope is similar to those observed for the other compounds reported here. Similarly, the area ratio, R , is temperature independent as noted above.

4. Summary and Conclusions

Seven ferrocenoid compounds in which one or more Cp ring protons have been replaced by electron-withdrawing C₆F₅ groups, have been investigated by temperature-dependent MES. It has been noted earlier in the literature¹⁶ that the electrochemical potentials for ferrocenes with a variable number of C₆F₅ substituents was a linear function of the number of such substituents. Consequently, it was expected that the IS parameter extracted from the MES data would show a similar linear correlation. However, as the data in Table 1 amply demonstrate, such a correlation is rather weak and shows only a small increase in IS(90) as the number of C₆F₅ groups (n) increases. Moreover, this increase – if real – would imply a smaller s-electron density at the Fe nucleus as n increases. The expectation here is that electron withdrawal by the C₆F₅ groups would decrease the d-electron shielding, and thus lead to an increase in the s-electron density and thus a decreasing IS(90). Clearly, the electron withdrawing effects of the C₆F₅ groups are more complex than this simplified picture predicts, and thus is worthy of further detailed study.

Finally, it should be noted that the agreement in the F factors between the X-ray and MES data in general is quite good, and that, as expected, the ratio of the X-ray to the MES value

increases from about 1.04 at 100 K to about 1.13 at 298 K reflecting the increasing influence of low-lying *intra*-molecular modes, such as ring rotations and librations and Cp-Fe-Cp deformation¹⁷ modes to the vibrations of the iron atom as T increases. In addition, these data clearly show that the iron atom motion in these complexes is predominantly isotropic in the temperature regimes employed in this study.

Acknowledgements. The authors are especially grateful to Prof. P. A. Deck for his generosity in providing the compounds examined in this study. The authors are indebted to Dr. S. Cohen for numerous fruitful discussions concerning the interpretation of the X-ray data reported in the literature. Thanks are also due to Prof. S. Biali for helpful discussions and graphic assistance.

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