The Mössbauer Effect and Chemistry. Part 9.[1] Molecular Motion in Solids. The Spectra of (η-Cyclohexatriene)(η-cyclopentadienyl)iron(II) Hexafluorophosphate

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The ^{57}Fe spectrum of the title cationic sandwich compound has been recorded at various temperatures in the range 4.2—350 K. At low temperatures it consists of a simple quadrupole doublet and a magnetically perturbed spectrum at 4.2 K reveals that V_{zz} is positive. At $T \geqslant 273$ K additional absorption to low energy is observed. As the temperature is increased a four-peak spectrum gradually develops which has an inner quadrupole doublet of magnitude approximately half that of the outer doublet. The spectrum is fully developed at 321 K but further heating brings about an inward collapse onto a single peak of much reduced intensity. This critical temperature is associated with a phase change of the solid. These processes are reversible. A model has been developed to account for the variation of spectrum with temperature. The organometallic cation is assumed to lie at an eight-co-ordinate site made up of eight PF_6 groups. At low temperatures the symmetry axis of the cation is collinear with the Z axis of the tetragon. As the temperature is raised, the X and Y orientations are Boltzmann populated and jump reorientations $X \longleftrightarrow Y$ take place at a significant rate giving rise to the inner doublet. These reorientations become faster with increasing temperature and on further heating those from $Z \longleftrightarrow X$ and $Z \longleftrightarrow Y$ become significant on the Mössbauer time scale and the spectrum becomes broadened and confused. Finally, all reorientations are so rapid that the cation is effectively spherical: this brings about a catharsis for the tetragonal phase in the form of a transition to one of cubic symmetry and the Mössbauer spectrum collapses to a narrow single peak.

MÖSSBAUER spectroscopy can be used to measure the energy difference between an excited nuclear state and its ground state.[2] If the environment of the nucleus is fluctuating then the spectrum is perturbed relative to the limits of fast or slow fluctuation. The first of these dynamic effects to be discovered was the second-order Doppler effect [3] which is manifest as a temperature shift of the resonance peak. It is caused by the random thermal motions of the atoms carrying the emitting or absorbing nuclei: for the ^{57}Fe resonance it gives rise to a shift in the absorption peak amounting to about one linewidth for a temperature change of 300 K. Some time later the gradual inward collapse of the characteristic six-line magnetic hyperfine pattern was attributed to the fluctuations in the magnetic field having reached a critical rate, that of the inverse of the lifetime of the excited nuclear state.[4] An analogue of this is the case where the electric-field-gradient (e.f.g.) tensor is fluctuating at this critical rate and this type of dynamic effect forms the subject of the present paper.

The effect of non-zero components in the e.f.g. tensor is to raise the degeneracy of those nuclear levels having the spin angular-momentum quantum number $I \geqslant 1$. For ^{57}Fe a doublet spectrum is associated with a resonating nucleus belonging to an iron atom lying at a non-cubic site. Cases where the e.f.g. tensor is fluctuating at a rate comparable with the inverse of the lifetime of the excited nuclear state are not common and it is normal practice in these studies, as in n.q.r. spectroscopy, to consider the e.f.g. tensor in the limit of fast relaxation at which all the molecular motions are time-averaged. The effects arising from a slowly fluctuating e.f.g. have been treated theoretically.[5] Here and elsewhere 'slowly' refers to a rate comparable, to within a few powers of ten, with $1/\tau_N$ ($\tau_N = 97.81$ ns) [6] where τ_N is the lifetime of the $I = \frac{3}{2}$ state of ^{57}Fe. A complete description of such a case has been given by Gibb,[7] that of the 3 : 1 clathrate of thiocarbonyl diamide and bis(η-cyclopentadienyl)iron(II), commonly called ferrocene. In this molecule, the iron atoms occupy sites of sufficiently low symmetry to give rise to an appreciable quadrupole splitting ($\Delta E = 2.381$ mm s^{-1}) although the molecules are approximately cylindrical and can therefore adopt various orientations in the channels of solid $CS(NH_2)_2$. Some of these orientations are more free to rotate than others and the nuclei embedded in the rotating molecules thus experience a slowly fluctuating e.f.g. The observed Mössbauer spectra are thereby different from those at the low-temperature limit at which the molecules are effectively frozen.

From the foregoing, it might be concluded that the case of this ferrocene clathrate is somewhat special, restricted in development, and limited in interest. This is not the case. Some years ago [8] we recorded some Mössbauer spectra of the sandwich compound (η-cyclohexatriene)(η-cyclopentadienyl)iron(II) hexafluorophosphate. Whilst the spectrum at 80 K was the expected quadrupole doublet, that recorded at 291 K contained additional absorptions to low energy. Following the publication of the paper on the ferrocene clathrate we speculated that the additional peaks could have arisen from molecular reorientation of the cation within the ionic matrix with this fulfilling the role of the channels of $CS(NH_2)_2$. This is indeed the case in this instance and for a number of other organometallic cations. In this paper we describe the behaviour of the title compound.

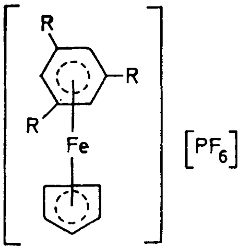
EXPERIMENTAL

(η-Cyclohexatriene)(η-cyclopentadienyl)iron(II) hexafluorophosphate was prepared using the method of Nesmeyanov *et al.*[9] as described by King [10] (Found: C, 38.35; H, 3.30; P, 8.75. $C_{11}H_{11}F_6FeP$ requires C, 38.4; H, 3.20; P, 9.00%). (η-Cyclopentadienyl)(η-1,3,5-trimethylcyclohexatriene)iron(II) hexafluorophosphate was prepared by the same procedure by substituting 1,3,5-trimethylcyclohexatriene for cyclohexatriene (Found: C, 43.05; H, 4.45; P, 8.15. $C_{14}H_{17}F_6FeP$ requires C, 43.55; H, 4.45; P, 8.00%).

Mössbauer spectra were recorded using an Elcint function generator in conjunction with a Meda 1024-channel multichannel analyser. The detector used was a Harwell Research proportional counter and the ^{57}Co(Pd) source was provided by the Radiochemical Centre, Amersham. Spectra were obtained using a conventional liquid nitrogen cryostat filled with water. A heater and electronic temperature controller ensured that the thermostatting was adequate and the lower temperatures were achieved using an external refrigerator. The magnetically perturbed Mössbauer spectra were obtained at 4.2 K using a B.O.C. SCM4 helium cryostat fitted with a superconducting magnet. Spectral data were processed using the CDC 6600 computer at London University and the IBM 360 computer at University College, London. A range of programs was used including that developed by Lang and Dale [11] for fitting magnetically perturbed spectra, and a number of relaxation programs similar to those outlined by Gibb [7] to which some fitting logic was added. Phase transitions were observed visually using a Reichert polarising microscope fitted with a hot stage, and *X*-ray powder photographs were obtained by Dr. R. S. Osborn at Imperial College through the U.L.I.R.S. scheme.

RESULTS AND DISCUSSION

The compounds to be discussed have the molecular structures (1). Cations of this type have been extensively studied.[12] Their method of preparation and their ^{1}H n.m.r. spectra [13] leave no doubt as to their sandwich nature, although no *X*-ray diffraction studies have been published. Various workers [14,15] have reported on Mössbauer spectra recorded at *ca.* 77, 200, and 300 K: no comment has been made on the anomalous nature of the spectrum of compound (1a) at 300 K and it seems that the spectral data were averaged for calculation of the conventional Mössbauer parameters. Thus, the workers in ref. 15 recorded the Mössbauer spectrum of compound (1a) at 300 K and gave a value of the quadrupole splitting of 1.217 mm s^{-1}. We found a spectrum consisting of two superimposed quadrupole doublets at 308 K which have an average splitting of 1.08 mm s^{-1}. Weighting of the outer peaks would increase this average to a value close to that quoted previously.



(1a) R = H
(1b) R = Me

Whilst ferrocene itself shows a quadrupole splitting of 2.381 mm s^{-1}, those measured for these cationic sandwich compounds are substantially lower, being 1.65 and 1.82 mm s^{-1} for compounds (1a) and (1b) respectively.

The greater part of the quadrupole splitting in ferrocene arises [16] *via* removal of electrons from the iron into the e_1 molecular orbitals on the cyclopentadienyl ring. These orbitals are fully occupied in cyclohexatriene and its derivatives and will therefore be less efficient in removing electron density from the metal.[17] This is reflected in a reduction in quadrupole splitting on passing from ferrocene to a cyclohexatriene–cyclopentadienyl iron compound. In ferrocene, the symmetry of the molecule demands that V_{ZZ}, the principal component of the e.f.g. tensor, is axially symmetric and coincident with the molecular axis. It is known to be positive. In the cases of compounds (1a) and (1b), the e.f.g. cannot be axially symmetric and we investigated this point further by measuring some magnetically perturbed Mössbauer spectra at 4.2 K, a technique which yields [2] a value of the asymmetry parameter η given by $(V_{XX} - V_{YY})/V_{ZZ}$. The observed spectra were fitted [11] to a Hamiltonian of the form (1), where Q is the electric quadrupole moment

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0 + \frac{eQV_{ZZ}}{4}\left[\hat{I}_z^2 - \frac{5}{4} + \frac{\eta}{3}(\hat{I}_x^2 - \hat{I}_y^2)\right] - g\mu_N IB \quad (1)$$

of the $I = \frac{3}{2}$ state of ^{57}Fe, I is the spin quantum number, μ_N is the nuclear magneton, g is the nuclear g factor, and B the magnetic flux density. The results of the best fit are shown in Table 1. The magnetically perturbed spectrum of compound (1b) together with its best fit is shown as Figure 1.

TABLE 1

Compound	B	ΔE_Q/ mm s^{-1}	δ_{Fe}/ mm s^{-1}	$\Gamma_{\frac{1}{2}}$	η
(1a)	3.11	1.64	0.54	0.36	0.3 ±0.2
(1b)	3.14	1.82	0.51	0.34	0.0 ±0.2

In both cases the results are unequivocal: V_{ZZ} is positive and the asymmetry parameter is sufficiently small for it to be neglected. At higher temperatures (*ca.* 300 K), free rotation of the carbocyclic ligands will almost certainly have set in and this will reduce the asymmetry parameter still further. It can also be assumed that V_{ZZ} coincides with the molecular axes of compounds (1). Having established that a molecule of near-axial symmetry is under investigation, consideration can now be given to the type of spectra which would arise if the e.f.g. were fluctuating due to molecular reorientation. Although these effects are probably not yet widely known, they have been the subject of much theoretical work [5,7] and it is only necessary to give a very brief outline of the theory and to present a few theoretical spectra to compare with our observed data.

The time-dependent Hamiltonian for a nucleus in an

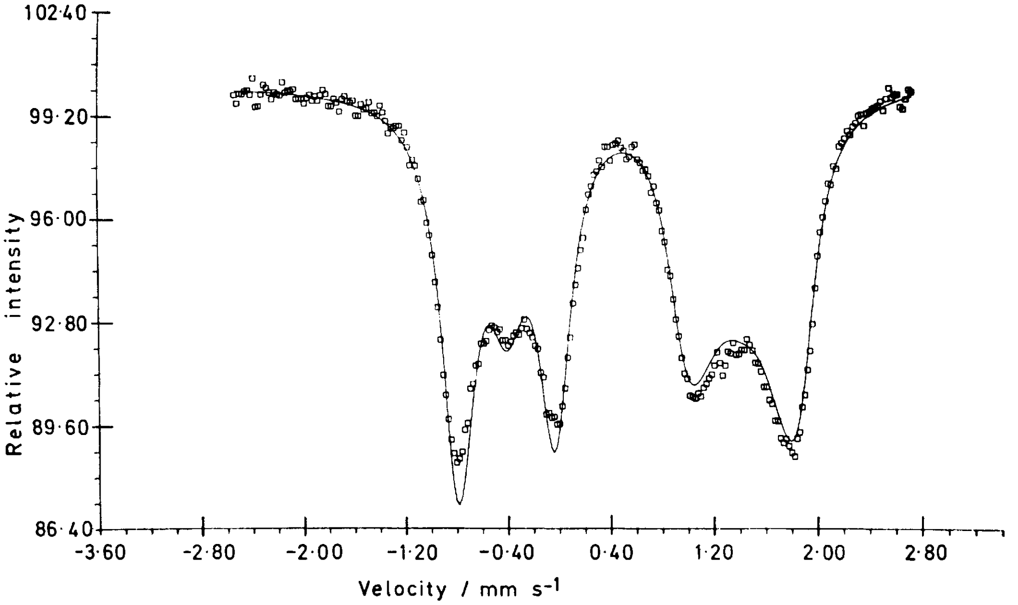


FIGURE 1 Mössbauer spectrum of compound (1b) at 4.2 K in a longitudinal magnetic flux of 3.14 T. The full curve represents the 'best fit' corresponding to the parameters in Table 1

environment where the principal component of an axially symmetric e.f.g. jumps at random between the x, y, and z axes of a frame of reference may be written as (2). $\hat{H}_0$

$$\hat{\mathscr{H}}_{(t)} = \hat{\mathscr{H}}_0 + [1 - \mathrm{f}^2(t)]\frac{\Delta_0}{6}(3\hat{I}_z^2 - I^2) + \tfrac{1}{2}\mathrm{f}(t)[1 + \mathrm{f}(t)]\frac{\Delta_0}{6}(3\hat{I}_x^2 - I^2) + \tfrac{1}{2}\mathrm{f}(t)[1 - \mathrm{f}(t)]\frac{\Delta_0}{6}(3\hat{I}_y^2 - I^2) \quad (2)$$

is the Hamiltonian for the nucleus in an isotropic electric field, $\Delta_0 = eQV_{ZZ}/2$ is the quadrupole splitting which would arise from the stationary interaction between the nucleus and the e.f.g., and f(t) is a random function such that we have equations (3)—(5). In these equations, I

$$\mathrm{f}(t) = 0 \quad \hat{\mathscr{H}}(t) = \hat{\mathscr{H}}_0 + \frac{\Delta_0}{6}(3\hat{I}_z^2 - I^2) \quad (3)$$

$$\mathrm{f}(t) = 1 \quad \hat{\mathscr{H}}(t) = \hat{\mathscr{H}}_0 + \frac{\Delta_0}{6}(3\hat{I}_x^2 - I^2) \quad (4)$$

$$\mathrm{f}(t) = -1 \quad \hat{\mathscr{H}}(t) = \hat{\mathscr{H}}_0 + \frac{\Delta_0}{6}(3\hat{I}_y^2 - I^2) \quad (5)$$

is the spin angular momentum quantum number and $\hat{I}_x$, $\hat{I}_y$, and $\hat{I}_z$ are quantum mechanical spin operators. The transition probabilities per unit time, W_{ij} for f(t) changing from value i to value j, are identifiable with the transition probabilities for the principal components of the electric field flipping from one orientation to another $W_{\pm} = W_{XY}$; $W_{+0} = W_{XZ}$; $W_{-0} = W_{YZ}$. These transition probabilities are inversely proportional to the correlation or relaxation time. The relaxation time of orientation i with respect to orientation j may be expressed in seconds as (6). For pure isotropic relaxation,

$$\tau_{ij} = 0.97 \times 10^{-7}(W_{ij})^{-1} \quad (6)$$

the populations of each molecular orientation, p_i, are equal and the matrix giving the Mössbauer lineshape is as in (7), where $\alpha = \Delta_0/4$. Numerical evaluation of $\tilde{G}(p)$ for different values of W corresponding to different

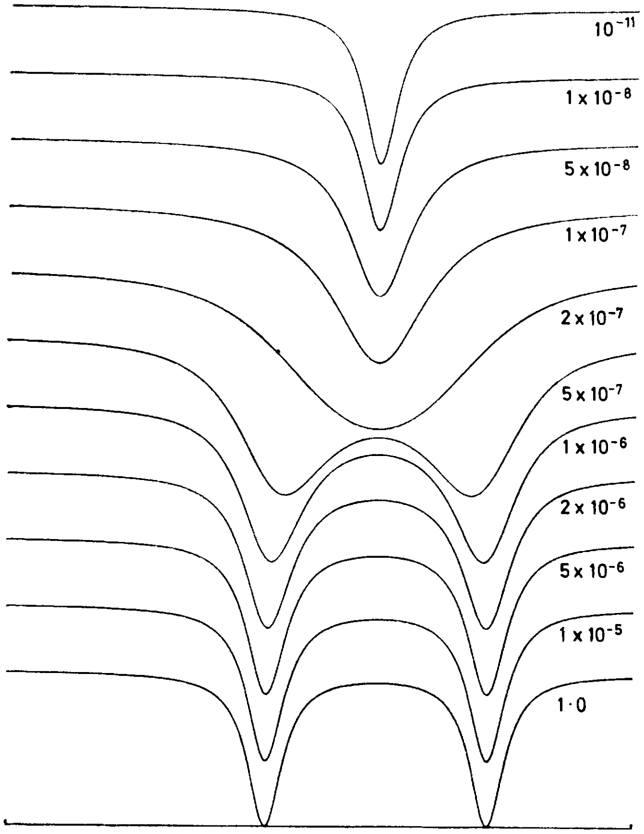


FIGURE 2 Effect of an isotropically relaxing e.f.g. on a quadrupole-split Mössbauer spectrum. Here $p_x = p_y = p_z = \frac{1}{3}$ and the single relaxation time τ_i/s is given for each curve

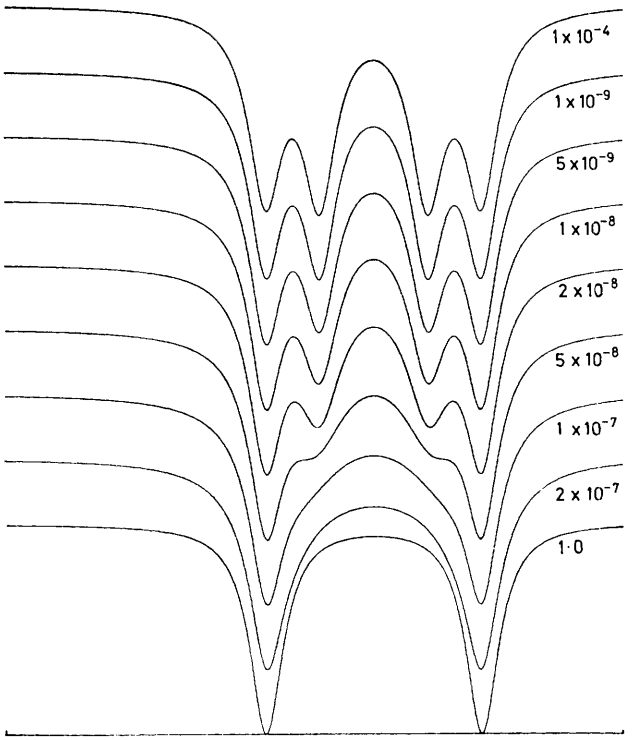


FIGURE 3 Effect of anisotropic relaxation in the XY plane. Here $p_x = p_y = 0.25$ and $p_z = 0.5$. The relaxation time τ_{XY}/s is given for each curve

relaxation times τ produces the curves shown in Figure 2. In the limit of slow relaxation, a simple quadrupole

$$\tilde{G}_{(p)} = \frac{p + 3W}{p^2 + 3pW + 4\alpha^2} \qquad (7)$$

doublet results whilst at the fast relaxation limit $\tilde{G}_{\infty}(p) = 1/p$ which gives a single Lorentzian of half-width Γ positioned at the centroid.

If the relaxation is anisotropic, there is a unique axis Z such that reorientation of the principal component of the e.f.g. from Z to X,Y has a different relaxation time for reorientations between X and Y: $W_{ZX} = W_{ZY} \neq W_{XY} = W_{YX}$. Under equilibrium conditions, the populations of each orientation of the e.f.g. may be such that $p_X = p_Y \neq p_Z$. The curves of Figure 3 have been produced by numerical evaluation of the appropriate expression for the intensity with $p_X = p_Y = 0.25$ and $p_Z = 0.5$. Here relaxation between the Z and X,Y axes is very slow and the effect of increasing X,Y relaxation is demonstrated for a range of τ_{XY}.

Under these conditions, at least half the Mössbauer nuclei retain an environment with an effectively stationary e.f.g. The outer doublet, with quadrupole splitting Δ_0, is associated with these nuclei. As the relaxation between the X and Y axes becomes faster, an inner doublet develops with the same centroid, sharpening in the limit of fast relaxation to the same linewidth as the outer doublet but with a splitting $\Delta_0/2$. At the limit of fast relaxation, this doublet can be visualised as arising from a charge array with circular symmetry. It is clear that the sign of the quadrupole splitting of the inner doublet will be opposite to that of the outer doublet.

The variation in Mössbauer spectrum with temperature for compound (1a) is shown in Figure 4. The low-temperature limit spectrum is a simple quadrupole doublet but from 273 K upwards the peaks are at first considerably broadened, then the growth of an inner quadrupole doublet takes place. These spectra are similar in outline to those shown in Figure 3. It is evident that anisotropic reorientation of the cation takes place over this temperature region. This was confirmed by carrying out an oriented absorber experiment. It proved difficult to grow good quality crystals of compound (1a) but some reasonable specimens were mounted as a partially oriented absorber, and a Mössbauer spectrum was recorded at room temperature. This is shown in Figure 5. Although this spectrum is not good, the intensity pattern is consistent with anisotropic reorientation.

Close inspection of Figure 4 and comparison of these spectra with those generated by the computer for pure anisotropic reorientation (Figure 3) reveals major discrepancies. The growth of the inner doublet is accom-

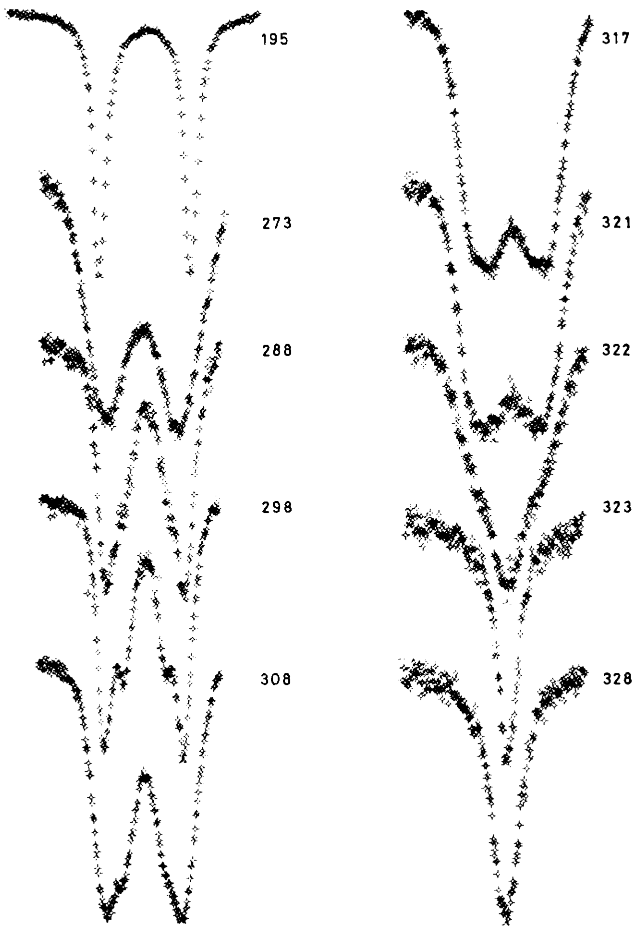


FIGURE 4 Mössbauer spectra of compound (1a) over the temperature range 195—328 K

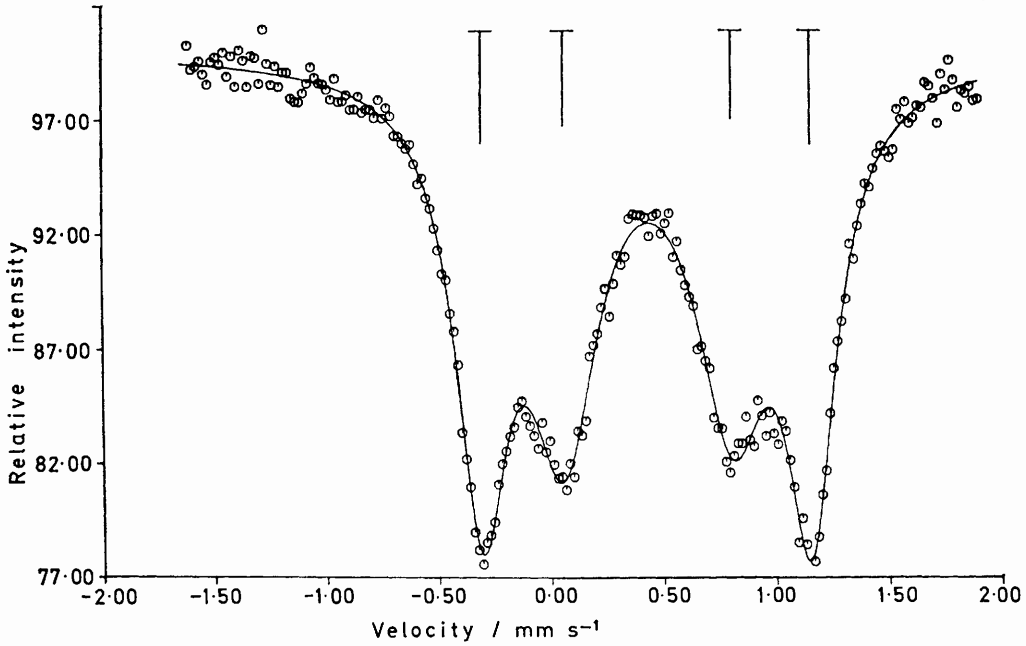


Figure 5 Mössbauer spectrum at 295 K of a partially aligned sample of compound (1a). The full curve is the best fit as determined by a least-squares program. A ' weak–strong–weak–strong ' intensity pattern is discernible

panied by a significant reduction in the splitting of the outer doublet (Table 2). Thus, the pure anisotropic rotational model is not appropriate and an alternative needs to be found. It is clear that the rotational processes are mixed in nature; rotation in the XY plane is accompanied by slower rotations in the ZX and ZY planes. This could arise if the organometallic cation occupies a tetragonal site made up of eight PF_6 groups. This siting would allow rotation in the XY plane to be easier than in the ZX and ZY planes. If the activation energies E_{XY} and E_{ZX}, E_{ZY} do not differ by too much, both types of rotational process would be operative at temperatures $T \gtrsim E/R$.

Table 2

Mössbauer spectral parameters (mm s^{-1}) obtained from spectral data for compound (1) by least-squares fitting

Compound	T/K	ΔE_Q	δ_{Fe} *
(1a)	78	1.65	0.52
	195	1.66	0.50
	273	1.58	0.45
		1.03	0.46
	288	1.46	0.44
		0.81	0.45
	308	1.45	0.44
		0.71	0.45
	321	1.46	0.44
		0.62	0.44
	323	0.0	0.43
	328	0.0	0.42
(1b)	78	1.82	0.53
	295	1.83	0.46

* Refers to the centre of the spectrum of a natural iron foil.

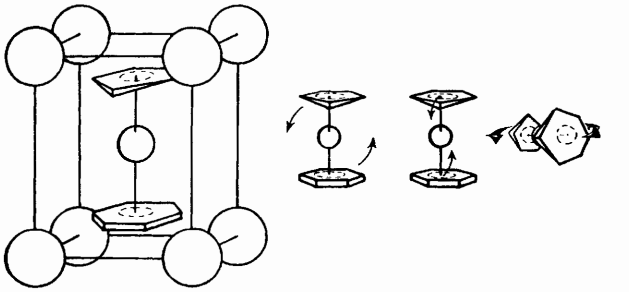


Figure 6 Schematic representation of the tetragonal-site model and its associated rotational processes. The organo-iron cation is surrounded by eight PF_6 groups

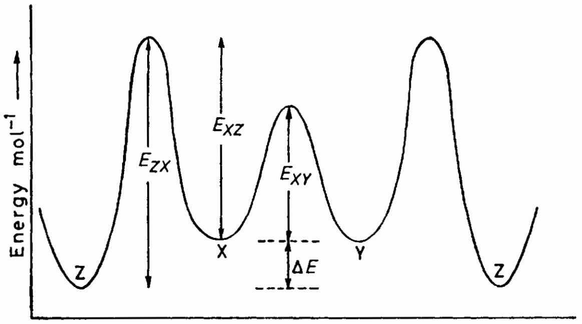


Figure 7 Potential-energy curve for rotation of compound (1b) within a tetragonal site. The three activation energies E_{ZX}, E_{XY}, and E_{XZ} are as indicated. ΔE (see text) is given by: $\Delta E = E_{ZX} - E_{XY}$

The tetragonal-site model is seen to be reasonable by analogy with the structure of $[Co(C_5H_5)(C_5H_4CO_2H)][PF_6]$ which displays this feature.[18] The structural model and the three rotational processes are illustrated diagrammatically in Figure 6. The associated potential-energy profile is shown in Figure 7. The system can be specified in terms of three activation energies E_{ZX}, E_{XZ}, and E_{XY} and two relaxation times τ_{XYO} and τ_{ZXO} such that $\tau_{ij} = \tau_{ijo}\exp(E_{ij}/RT)$. The populations p_i may be written as in equations (8) and (9).

Using these expressions for the populations, a set of spectra were generated using the expression for $\tilde{G}(p)_{xy}$

given in ref. 7. The addition of fitting logic to this program enables a set of ' best-fit ' values for the five

$$p_x = p_y = \frac{\exp(-\Delta E/RT)}{1 + 2\exp(-\Delta E/RT)} \qquad (8)$$

$$p_z = \frac{1}{1 + 2\exp(-\Delta E/RT)} \qquad (9)$$

parameters to be extracted. In practice, it proved difficult to achieve a good fit and it was necessary to set τ_{ZXO} and τ_{XYO} to the same fixed value, that of 10^{-10} s found by Gibb for the ferrocene–$CS(NH_2)_2$ system. Even then, the fit we achieved leaves something to be desired; it is illustrated in Figure 8, the caption of which lists the corresponding values of E_{ij}. The tetragonal-site model is plausible but an alternative model involving a second-order phase transition over the range 288—321 K is not excluded. This phase transition could be associated with the gradual onset of rotation $Z \rightarrow X$, $Z \rightarrow Y$, and $X \rightarrow Y$ and would involve variable activation energies. The tetragonal-site model is inadequate at the high-temperature limit. There is a phase change at 319 K which can be observed with the naked eye under a polarising microscope fitted with a hot stage. Since the polarising colours disappear completely at that temperature, it is reasonable to conclude that the crystal has undergone a transition to cubic symmetry. The tetragonal site will disappear with such a transition, rotation can take place in all directions, and a Mössbauer spectrum of just a single peak is observed. The *X*-ray powder photographs recorded above and below the transition temperature are different. It may be that the crystal is non-cubic below the transition temperature as a consequence of the cylindrical nature of the cation. As the temperature is raised, some molecules begin to rotate but the majority remain frozen. With further increase in temperature rotational lawlessness becomes co-operatively widespread and the complete breakdown is reached with a phase transition at which point the cation has become effectively spherical and the need for the low-symmetry phase has gone. These rotational processes are sensitive to substituent; the mesityl derivative, compound (1b), shows no evidence of rotation at 295 K indicating that the introduction of the methyl groups has sterically hindered the rotational processes.

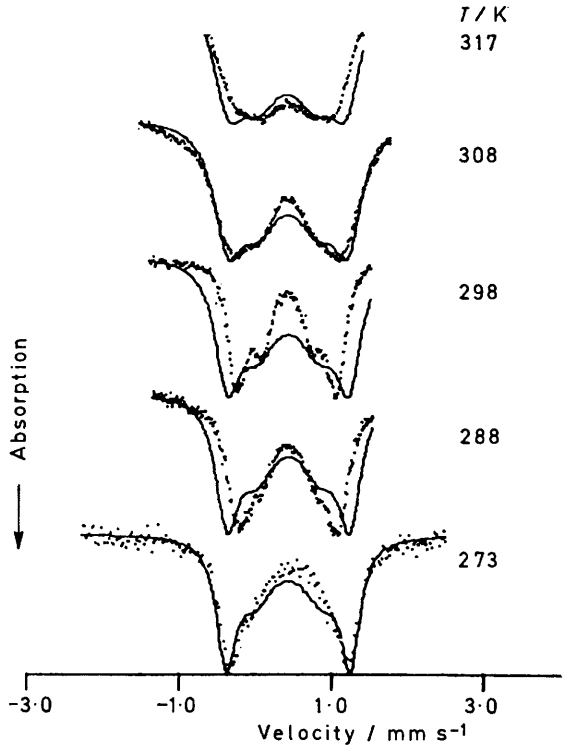


FIGURE 8 Representative attempt to obtain a ' least-squares ' fit between the Mössbauer spectra for compound (1a) and the tetragonal-site model. The full curves are calculated using the following parameter values: $E_{ZX} = 20.0$, $E_{XY} = 10.0$, $E_{XZ} = 18.0$ kJ mol^{-1}, $\tau_{XYO} = \tau_{XZO} = 4 \times 10^{-10}$ s

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REFERENCES

[1] Part 8, B. W. Fitzsimmons and A. R. Hume, *J.C.S. Dalton*, 1979, 1548.

[2] N. N. Greenwood and T. C. Gibb, ' Mössbauer Spectroscopy,' Chapman and Hall, London, 1971; T. C. Gibb, ' The Principles of Mössbauer Spectroscopy,' Chapman and Hall, London, 1976.

[3] B. D. Josephson, *Phys. Rev. Letters*, 1960, **4**, 274.

[4] M. Blume, *Phys. Rev.*, 1968, **174**, 351.

[5] J. A. Tjon and M. Blume, *Phys. Rev.*, 1968, **165**, 456.

[6] ' Mössbauer Effect Data Index 1972,' eds. J. G. Stevens and V. E. Stevens, Adam Hilger, London, 1973.

[7] T. C. Gibb, *J. Phys. (C), Solid State*, 1976, 2627.

[8] N. J. Seeley, Ph D., Thesis, University of London, 1970.

[9] A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Tetrahedron Letters*, 1963, 1725.

[10] R. B. King, *Organometallic Synth.*, 1965, **1**, 138.

[11] G. Lang and B. W. Dale, U.K.A.E.W. Research Group Report, ' Program for Least-Squares Fitting of Mössbauer Spectra in Applied Fields,' U.K.A.E.W., Harwell, 1973.

[12] W. E. Silverthorn, *Adv. Organometallic Chem.*, 1975, **13**, 47.

[13] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.* (*C*), 1968, 2257.

[14] K. I. Turta, R. A. Stuken, V. I. Gol'danskii, N. A. Vol'kenau, N. A. Sirotkina, I. N. Bolesova, L. S. Iseva, and A. N. Nesmeyanov, *Teor. i eksp. Khim.*, 1971, **7**, 486.

[15] R. B. King, L. M. Epstein, and E. W. Gowling, *J. Inorg. Nuclear Chem.*, 1970, **32**, 441.

[16] R. L. Collins, *J. Chem. Phys.*, 1965, **42**, 1072.

[17] S. E. Evans, J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1974, 304.

[18] P. E. Riley and R. E. Davis, *J. Organometallic Chem.*, 1978, **152**, 209.