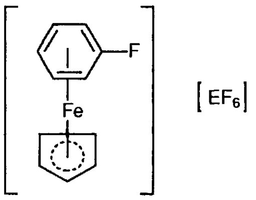
Molecular Motion in Solids. The Mössbauer Spectra of (η-Cyclopentadienyl)(η-fluorobenzene)iron(II) Salts

Brian W. Fitzsimmons * and **Ian Sayer**
Department of Chemistry and Biological Chemistry, The University of Essex, Wivenhoe Park, Colchester, CO4 3SQ, UK

The ^{57}Fe Mössbauer spectra of [Fe(η-FC$_6$H$_5$)(η-C$_5$H$_5$)]A (A = PF$_6$, AsF$_4$, SbF$_6$ or BF$_4$) have been recorded at various temperatures in the range 77–350 K. That of the hexafluorophosphate salt is a quadrupole doublet which broadens above 228 K, coalesces at 240 K, and is fully narrowed at 300 K. This is interpreted in terms of isotropic reorientation of the cation. Fitting of the spectral results by an appropriate model yields an activation energy of 19.6 kJ mol^{-1} for this process. X-Ray diffraction results obtained at 300 K indicate a primitive cubic cell of side 6.9 Å with totally disordered cations. There is a first-order phase transition at 225 K which heralds the onset of rotation. The AsF$_6^-$ and SbF$_6^-$ salts display analogous behaviour but the spectrum of the BF$_4^-$ salt is a simple quadrupole doublet over the entire temperature range.

It is becoming increasingly evident that groups of atoms in some solids can undergo more extensive motion than is implicit in the traditional picture of small oscillations about equilibrium positions.[1] Plastic crystals such as camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one) or adamantane (tricyclo[3.3.1.1^{3,7}]-decane) are extreme cases; here, whole-body tumbling is dominant and it confers a special behaviour type which is well documented.[2] However, there are many cases in which spectral or thermodynamic properties are strongly affected by large-amplitude oscillations or rotations in solids which retain sufficient rigidity so as to preclude plastic flow. Chemical reactions such as polymerisation or isomerisation can originate in these reorientational processes and solving crystal structures by X-ray diffraction can be seriously hampered by their presence.[3] Thus, there is an incentive to study these anarchic regimes: we are interested in them as potential materials in molecular electronics and are looking for ways to switch between ordered and disordered states. Our principal tool continues to be Mössbauer spectroscopy with differential scanning calorimetry (DSC) as a detector of phase transitions.

If an iron-containing molecule undergoes jump reorientation such as to relabel Cartesian axes having the iron nucleus as origin, then any quadrupole splitting in its Mössbauer spectrum will be modified relative to fast or slow relaxation limits. This provides a method of detecting and studying these reorientational processes. The theoretical basis of electric field gradient relaxation was investigated some time ago.[4–6] More recently, a number of examples of systems displaying this feature have been unearthed. The best known of these and the one closest to what we describe here is that of the 3:1 thiourea–ferrocene clathrate.[7] Here, the approximately cylindrical ferrocenes can adopt various orientations in the channels of the host lattice with some being more prone to reorientation than others. The observed Mössbauer spectra are thus strongly temperature dependent and they have been fully analysed. A further instance is provided by the ferrocene α- or β-cyclodextrin inclusion compounds.[8] Reorientation of the ferrocenes within the cyclodextrin cavities gives rise to temperature-dependent spectra showing quadrupole relaxation. The Mössbauer lattice temperature of ferrocene in β-cyclodextrin is markedly lower than that of polycrystalline ferrocene.[9] Jump reorientation of one of the carbonyl groups about a three-fold axis in the tetracarbonylhydridoferrate(2−) ion has also been shown to be a case where quadrupole splitting is modified by dynamic processes.[10] We have described the dynamic processes in the salt [Fe(C$_6$H$_6$)(C$_5$H$_5$)]PF$_6$ in which anisotropic reorientation was dominant.[1] This paper is about these processes in the fluorobenzene–cyclopentadienyl mixed-sandwich species **1** which exhibit quite different behaviour despite the close similarity in structure.



	E
1a	P
1b	As
1c	Sb

Experimental

(η-Cyclopentadienyl)(η-fluorobenzene)iron(II) salts were prepared following the published procedures[11] (Found for the PF$_6$ salt: C, 36.6; H, 3.05. C$_{11}$H$_{10}$F$_7$FeP requires C, 36.50; H, 2.80. Found for the AsF$_6$ salt: C, 36.6; H, 3.05. C$_{11}$H$_{10}$AsF$_7$Fe requires C, 32.55; H, 2.50. Found for the SbF$_6$ salt: C, 29.85; H, 2.45. C$_{11}$H$_{10}$F$_7$FeSb requires C, 29.10; H, 2.40. Found for the BF$_4^-$ salt: C, 43.65; H, 3.00. C$_{11}$H$_{10}$BF$_5$Fe requires C, 43.50, H, 2.30%). ^{1}H NMR of [Fe(FC$_6$H$_5$)(C$_5$H$_5$)]$^+$: δ 6.84 (t, phenyl protons H^1,H^5), 6.60 (m, H^2, H^4) 6.40 (m, H^3), and 5.36 (s, cyclopentadienyl protons). The spectra were unaffected by the anions. Principal infrared maxima for the PF$_6$ salt: 3120, 3100, 1530, 1462, 1239, 1140, 1012, 835 and 560 cm^{-1}. The AsF$_6$ and SbF$_6$ salts have similar spectra except for EF$_6$ peaks at 669, 399 and 660, 290 cm^{-1} respectively replacing those at 835 and 560 cm^{-1} for the PF$_6$ salt. Peaks for the BF$_4$ salt are at 3100, 3040, 2960, 2920, 2860, 1530, 1462, 1420, 1235, 1060, 482 and 462 cm^{-1}. Mössbauer spectra were recorded using a microprocessor-based constant-acceleration spectrometer supplied by Cryophysics (UK) Ltd. The detector used was a Harwell Research proportional counter and the ^{57}Co(Pd) source was supplied by Amersham International. Spectral data were processed using the CDC 6600 computer at London University. A range of programs was used including some relaxation programs

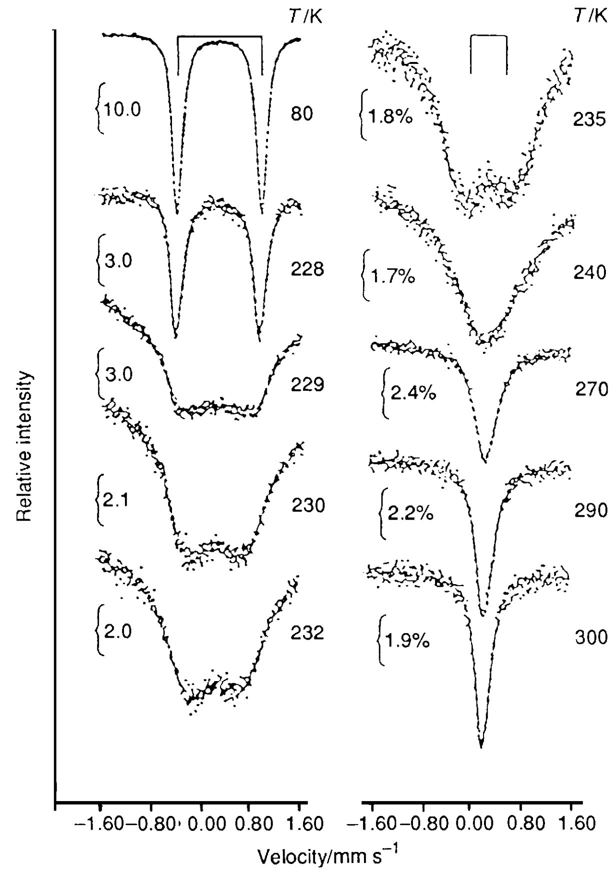


Fig. 1 Iron-57 Mössbauer spectra of compound **1a**

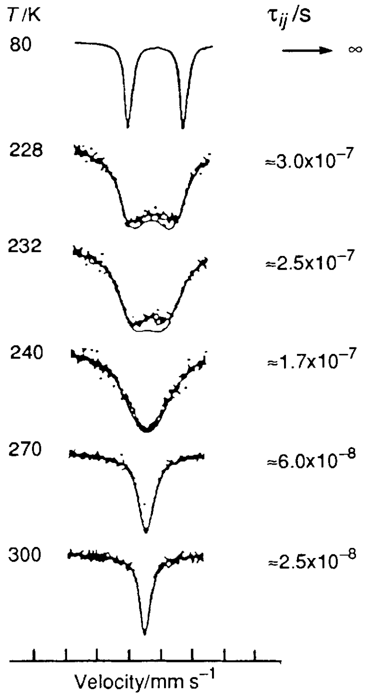


Fig. 2 Least-squares fits of Mössbauer spectra of compound **1a** by theoretical spectra for isotropic reorientation with correlation times indicated

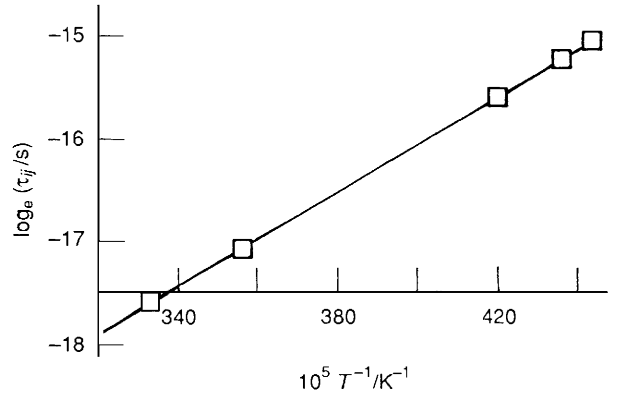


Fig. 3 Arrhenius plot of $\log_e(\tau_{ij})$ *vs.* $1/T$ for compound **1a**

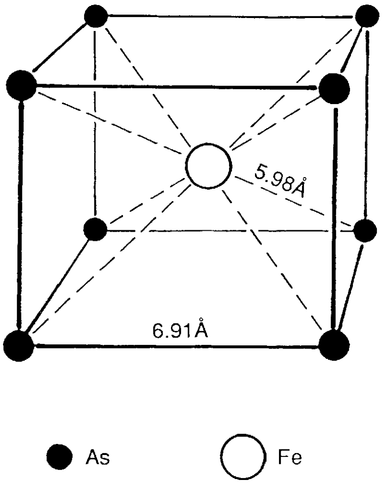


Fig. 4 The unit cell of compound **1b**. Those of compounds **1a** and **1c** are similar

described by Gibb[7] but with some fitting logic added. Thermal properties were investigated using a differential scanning calorimeter (Perkin-Elmer DSC 1-B). Temperature scans were made in the range between 200 K to just below the decomposition point with 8 °C min^{-1} heating and cooling rate. X-Ray diffraction results were obtained by Dr. A. M. R. Galas and Professor M. B. Hursthouse at the X-ray Crystallographic Unit at Queen Mary and Westfield College, London.

Proton NMR spectra were recorded in $[^2H_6]$acetone solution using a JEOL FX-200 spectrometer.

Results and Discussion

The Mössbauer spectra of compound **1a** are shown in Fig. 1. The normal quadrupole doublet observed at low temperatures gradually gives way to a singlet as the temperature is raised. There is a marked fall in recoil-free fraction as the high-temperature phase is attained. The spectrum is fully narrowed at 300 K. The anomalous temperature dependence of the spectrum of this compound has been noted before[12] and an explanation in terms of reorientational motion was put forward but not fully developed.[13] The behaviour from coalescence up to the high-temperature limit is well matched by the theoretical spectra computed for the isotropic rotational model (see Appendix). At the high-temperature limit, rotation of the molecules about their iron nuclei is fast compared with 10^{-7} s and the quadrupole splitting is vanishingly small. Fitting the experimental results to the theoretical curves yields values for the correlation times τ_{ij} (Fig. 2) and a plot of log τ_{ij} against $1/T$ is linear with $\tau_0 = 1.8 \times 10^{-8}$ s and $E_{ij} = 19.6$ kJ mol^{-1} (Fig. 3). X-Ray diffraction results obtained at 300 K indicate a primitive cubic cell of side 6.9 Å with cations totally disordered (Fig. 4). The cell dimensions of the AsF_6 and SbF_6 salts are equal to this and to one another. Compounds **1b** and **1c** show essentially similar behaviour. Differential scanning calorimetry (DSC) thermograms are consistent with first-order phase transitions at 225 K for these three compounds. The hysteresis is about 10 K. Compound **1d** displays a normal quadrupole splitting over the entire temperature range and no phase transition is evident. The

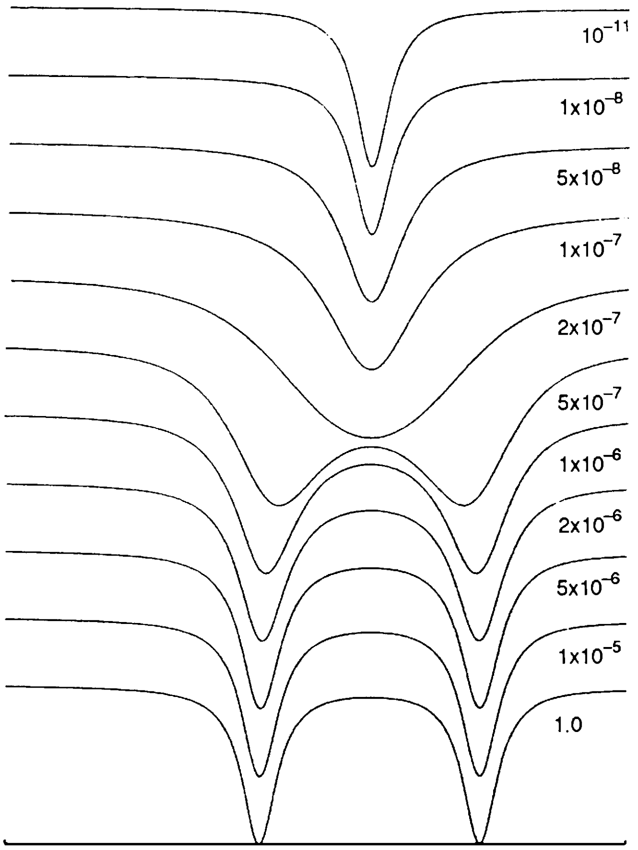


Fig. A1 Effect of an isotropically relaxing electric field gradient on a quadrupole-split Mössbauer spectrum. The single correlation time τ/s is given for each curve

transition temperatures and enthalpies ($\approx$ 3 kJ mol^{-1}) are the lowest of all the compounds of this type so far studied. Thus the PF_6 salts of this cation cross a phase barrier at 225 K to adopt isotropic rotational phases of cubic crystallographic symmetry. The BF_4 anion does not have this effect upon its cation partner. Below T_c, compounds **1a**–**1c** might adopt the more tightly packed rock salt structure in which cation reorientation is less likely. The substitution of fluorine by hydrogen in compound **1** gives salts with higher transition temperatures[1] ($T_c \approx 270$ K). It is tempting to speculate that the replacement of hydrogen by fluorine has little steric consequence but it provides an electric dipole to which local oscillating dipoles can effectively couple, thus precipitating rotational lawlessness at significantly lower temperatures than in the unsubstituted compound. In this series of compounds, the BF_4 anion does not have the power to induce reorientational processes.

What we have here is a phenomenon which is relatively straightforward in description whilst the underlying mechanisms remain obscure. However, by varying the arene substituents, we have made some examples which display isotropic reorientation and we are experimenting further with them.

Appendix

A very brief outline of the Tjon–Blume[4,5] and Gibb[7] treatment of isotropic electric field gradient relaxation is included here. The time-dependent Hamiltonian for a nucleus in an environment where the principal component of an axially symmetric electric field gradient jumps at random between the x, y, and z axes may be written as in equation (A1) where H_0 is the

$$H_{(t)} = H_0 + [1 - f^2(t)]\frac{\Delta_0}{6}(3I_z^{\,2} - I^2) + \tfrac{1}{2}f(t)[1 + f(t)]\frac{\Delta_0}{6}(3I_x^{\,2} - I^2) - \tfrac{1}{2}f(t)[1 - f(t)]\frac{\Delta_0}{6}(3I_y^{\,2} - I^2) \quad \text{(A1)}$$

Hamiltonian for the nucleus in an isotropic electric field, $\Delta_0 = eQV_{zz}/2$, the stationary quadrupole splitting, and $f(t)$ is a random function of time with values of 0 and ±1. The transition probabilities per unit time, W_{ij} for $f(t)$ changing from value i to value j are the transition probabilities for the principal components of the electric field gradient flipping from one orientation to another, *e.g.* $W_{\pm} = W_{xy}$, *etc.* Numerical evaluation of G(p) for different values of W corresponding to different correlation times τ [$\tau_{ij} = 0.97 \times 10^{-7}\ (W_{ij})^{-1}$] produces the curves shown in Fig. A1.

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