Molecular Motion in Solids: Mossbauer Spectra of $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)][AsF_6]$

Brian W. Fitzsimmons and William G. Marshall
Department of Chemistry and Biological Chemistry, the University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK

The ^{57}Fe Mossbauer spectrum of the compound $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)][AsF_6]$ has been recorded in the temperature range 77–315 K. At low temperatures the spectrum is the expected quadrupole doublet but as the temperature is raised a new doublet gradually develops in the centre of the absorption. This feature is fully developed at 312 K. A relaxation model based on anisotropic reorientation of the sandwich cations within a monoclinic lattice is put forward.

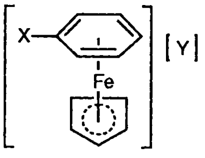
Since the first preparation and characterization[1] of the mixed sandwich cationic compound $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$, many further examples have been prepared, their physical and chemical properties investigated[2,3] and several crystal and molecular structures determined.[4] We have reported on the large-amplitude reorientational motion that is active in the crystalline hexafluorophosphate **1a**.[5] This reorientational motion corresponds to rotations in the *xy*, *zx* or *zy* planes of the crystal and as such is readily detected with the aid of Mössbauer spectroscopy if and when the reorientational rate is close to the reciprocal of the quadrupole precession time. It is quite distinct from the better known rotational reorientation about the *z* axis known to take place in ferrocenes.[6] This process is not expected to have a major effect upon the Mossbauer spectrum. The fluorobenzene derivatives **1b** differ significantly from the unsubstituted compound **1a** in that the reorientational motion is isotropic and sets in at a lower temperature.[7] The half-sandwich compound **2** shows isotropic reorientation which sets in abruptly at 250 K but the Mössbauer spectrum above this temperature contains no useful information.[8] In all these cases, the fluoroanions BF_4^- and EF_6^- (E = P, As or Sb) are implicated in co-operative breakdown of order in that these effects have not been observed in salts containing simple anions or complex anions without fluorines bonded to the central atom. It seems that such anions do not have the necessary properties to induce rotational disorder.

Our understanding of the ways in which the molecular motion modifies the quadrupole splitting in the Mössbauer spectrum is based on the classic case of the tumbling of ferrocene molecules in the hexagonal channels in the thiourea–ferrocene 3:1 clathrate. This system was successfully interpreted in terms of relaxation theory and the original paper includes theoretical spectra for various cases of interest as well as providing the means of calculating them.[9]

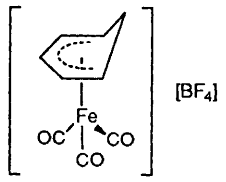
Disorder can have a direct impact upon the solution of X-ray diffraction data for crystals in which it is active.[10] In this paper we describe the strongly anisotropic reorientation in the compound **1c** for which we have a structural model obtained by X-ray methods which is in complete agreement with the Mössbauer spectral results.

Experimental

(η-Benzene)(η-cyclopentadienyl)iron(II) hexafluoroarsenate was prepared as follows. Ferrocene (9.3 g, 0.05 mol), powdered aluminium metal (1.35 g, 0.05 mol) and anhydrous aluminium chloride (20 g, 0.15 mol) were warmed to reflux with stirring in a nitrogen atmosphere. Water (0.9 g, 0.05 mol) was added and the mixture refluxed for 12 h. The cold mixture was hydrolysed carefully by the dropwise addition of water (100 cm^3). The dense yellow-green aqueous layer was separated, washed with benzene and filtered directly into a cold stirred solution of ammonium hexafluoroarsenate (3 g in 25 cm^3 water). The resulting yellow powder was filtered off and purified by dissolution in acetone and reprecipitation by water before being recrystallized from acetone. Yield 40% (Found: C, 34.20; H, 2.90. $C_{11}H_{11}AsF_6Fe$ requires C, 34.05; H, 2.85%). ^1H NMR spectrum: δ 6.48 (C_6H_6) and 5.24 (C_5H_5). Principal infrared peaks at 3120, 3100, 1450, 1422, 1162, 1120, 1015, 699, 485 and 470 cm^{-1}.



	X	Y
1a	H	PF_6
1b	F	PF_6, AsF_6, or SbF_6
1c	H	AsF_6



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Mossbauer spectra were recorded using a microprocessor-based constant-acceleration spectrometer supplied by Cryophysics (UK). 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 as described by Gibb[9] but with some fitting logic added. Thermal properties were investigated using a differential scanning calorimeter (Perkin-Elmer DSC-1). Temperature scans were made in the range between 200 K to just below the decomposition point with heating and cooling rates of 8 K min^{-1}. X-Ray diffraction results were obtained by Drs. R. A. Palmer and B. Etemadi in the Department of Crystallography, Birkbeck College, University of London, and will be published in full elsewhere.[11] Proton NMR spectra were recorded in $(CD_3)_2CO$ solution using a JEOL FX-200 spectrometer.

Results and Discussion

Some representative Mossbauer spectra of compound **1c** are shown as Fig. 1. At 77 and up to 270 K the spectrum is the normal quadrupole doublet as expected for this and related compounds. Differential scanning calorimetry reveals a first-

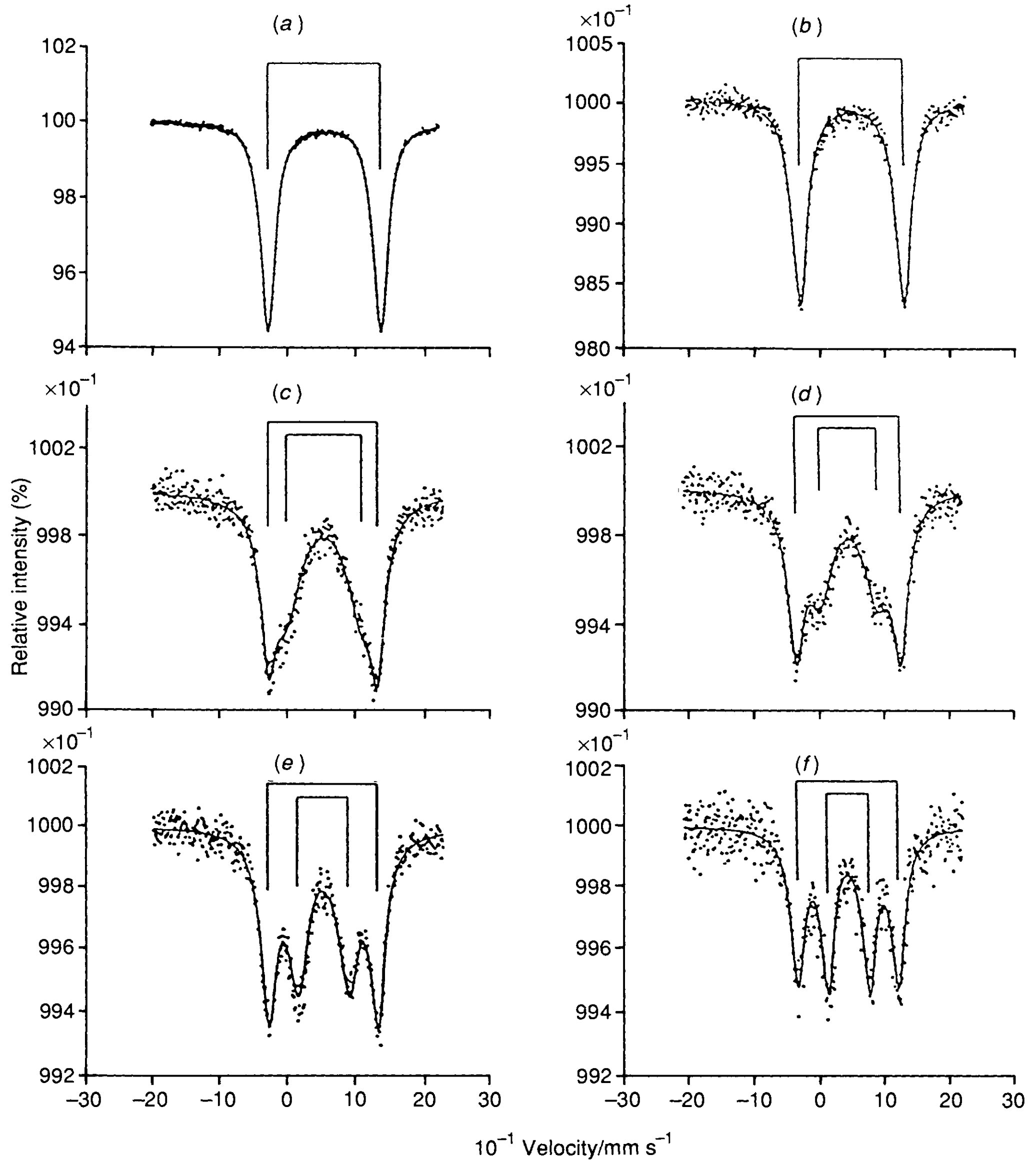

Fig. 1 Representative Mössbauer spectra of compound **1c** at 77 (*a*), 270 (*b*), 275 (*c*), 277 (*d*), 280 (*e*) and 310 K (*f*)

order phase transition at 265 K. This is the transition to the monoclinic phase in which the rotational disorder is active and detected through the changes in the Mössbauer spectra. An inner pair of resonance lines gradually emerge and this feature is fully developed at 310 K. In all, some nineteen spectra were collected and fitted using a least-squares procedure. The fitted parameters are collected in Table 1. This temperature dependence is characteristic of anisotropic reorientation of the cations within a lattice generated by the hexafluoroarsenate anions. It may be viewed in terms of a solid comprising two distinct anion–cation sets with each set of cations lying at the bottom of energy wells of different depths. The presence of two distinct sets of molecules within the crystal is confirmed by a structure determination. The cell is monoclinic with space group *Ia* and $a = 9.680$, $b = 9.660$, $c = 27.506$ Å, $\beta = 93.84°$ and $Z = 8$ (Fig. 2). There are two molecules in the asymmetric unit with one showing some rotational disorder and the other ordered and well behaved. These are the two cation sets referred to above. There is similar disorder in the anion lattice.

At low temperatures, under the influence of modest thermal energies, these cations rock gently about their centres. As the temperature is raised, the rocking motion becomes more pronounced with some of the cations facing the lower barrier now able to cross it. With rising temperature increasing numbers of the disorderly cations make the crossing and a new electric field gradient is set up with its major component perpendicular to that of the static molecule. In the limit of fast relaxation a two-doublet spectrum is the result. The outer doublet arises from the cations facing the higher energy barrier and the inner doublet arises from the cations in rapid transit across the lower barrier. The iron nuclei in these cations experience a well defined electric field gradient approximately one-half the magnitude of that in the static molecule.

Provided that the energy barriers are appreciably different, then the expected quadrupole splitting ratio in the two-doublet spectrum is 2:1. Inspection of the results in Table 1 reveals that there are departures from ideal behaviour in that this ratio is not exactly observed. The quadrupole splitting of the inner doublet does not converge to a value of 0.829 mm s^{-1} as required for a pure anisotropic system. It decreases with rising temperature to a value of 0.631 mm s^{-1}. We considered small departures from ideality. First, two relaxation times τ_{xy} and τ_{yx} for the reorientation in the *xy* plane were introduced: that is, some degree of anisotropy is associated with this motion. Whilst this

Table 1 Computed fits to Mossbauer spectral data for compound **1c** at the temperatures indicated

T/K	Isomer shift/mm s^{-1}	Half width/mm s^{-1}	Quadrupole splitting/mm s^{-1}	Ratio*
77.3	0.5403(3)	0.1300(5)	1.658(1)	—
77.3	0.5345(6)	0.1416(11)	1.649(1)	—
85.0	0.5385(8)	0.1362(15)	1.657(2)	—
95.1	0.5361(4)	0.1311(8)	1.654(1)	—
105.0	0.5332(5)	0.1288(9)	1.654(1)	—
125.0	0.5266(10)	0.1436(20)	1.649(2)	—
150.0	0.5198(6)	0.1342(12)	1.646(1)	—
175.0	0.5130(10)	0.1316(20)	1.645(2)	—
200.0	0.5007(8)	0.1331(16)	1.634(2)	—
225.0	0.4911(7)	0.1323(17)	1.615(2)	—
250.0	0.4813(8)	0.1336(16)	1.584(2)	—
270.0	0.4814(9)	0.1411(18)	1.571(2)	—
275.0	0.4686(21)	0.1225(71)	1.602(7)	0.689(17)
	0.4857(39)	0.2642(140)	1.104(27)	
277.5	0.4638(21)	0.1398(54)	1.579(6)	0.545(10)
	0.4697(46)	0.2309(103)	0.860(15)	
280.0	0.4653(18)	0.1346(38)	1.595(4)	0.464(4)
	0.4665(26)	0.1799(47)	0.740(6)	
295.2	0.4449(22)	0.1267(44)	1.564(45)	0.421(3)
	0.4433(25)	0.1439(44)	0.659(5)	
300.0	0.4392(24)	0.1241(50)	1.562(5)	0.415(4)
	0.4396(28)	0.1447(48)	0.649(6)	
305.0	0.4393(25)	0.1340(53)	1.552(5)	0.411(4)
	0.4385(28)	0.1475(49)	0.638(6)	
310.0	0.4362(31)	0.1291(63)	1.530(6)	0.412(4)
	0.4439(31)	0.1276(53)	0.631(6)	

Relative to metallic Fe at T 298 K.

* The quadrupole splitting ratio $\Delta_{inner}/\Delta_{outer}$.

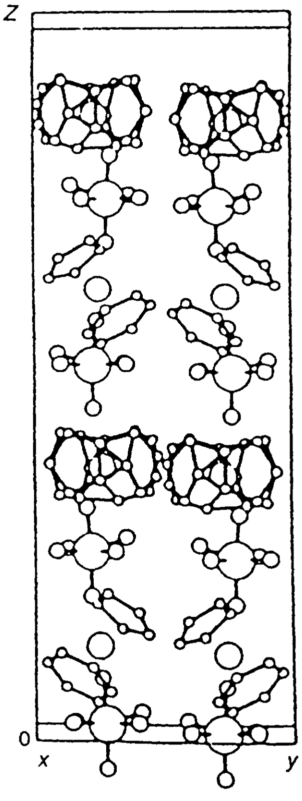

Fig. 2 Unit cell of the monoclinic phase of compound **1c**. Of the eight molecules in the unit cell, four are disordered through rotations in the xy plane

made a marginal improvement, the fit between the calculated and observed spectrum is not good enough (Fig. 3). A more successful model was developed by adding slow jumps from the xy plane to z. This will clearly have the effect of lowering the

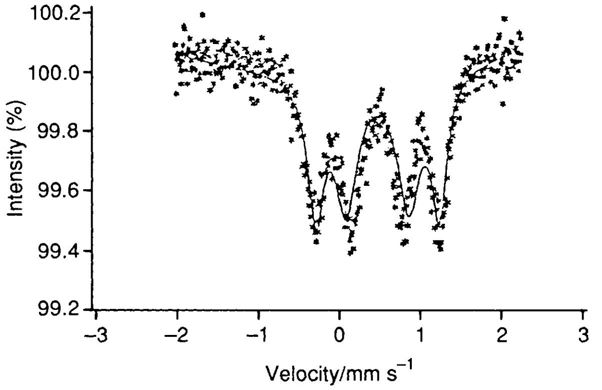

Fig. 3 Attempted fit of the spectrum of compound **1c** at 305 K assuming anisotropic xy reorientation with $\tau_{xy} = 1.2 \times 10^{-8}$ s and $\tau_{yx} = 1.1 \times 10^{-8}$ s

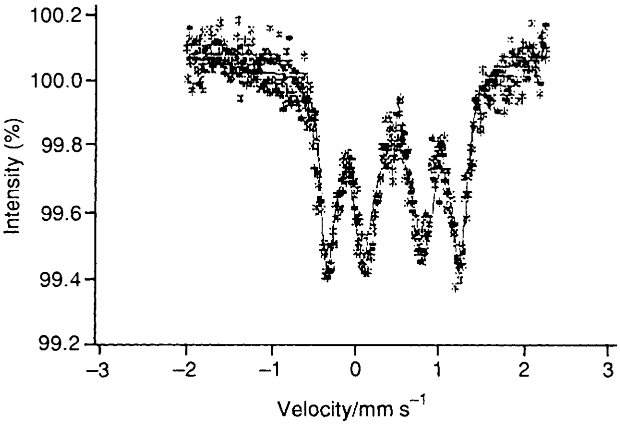

Fig. 4 Fit of the spectrum of compound **1c** at 300 K to a reorientational model including slower jumps $x \longrightarrow z$: $\tau_{xy} = 1.0 \times 10^{-8}$ s and $\tau_{xz} = 1.0 \times 10^{-4}$ s

quadrupole splitting associated with the *xy* molecules. The fit is shown in Fig. 4. With $\tau_{xy} \approx 10^{-8}$ s and $\tau_{xz} \approx 10^{-4}$ s, the agreement is very good. Values of the relaxation times τ_{xy} were derived assuming a purely anisotropic system. Assuming also an Arrhenius temperature dependence, $\tau_{xy0} \approx 2 \times 10^{-9}$ s and $E_{xy} \approx 29$ kJ mol^{-1}. These can be compared with 1.8×10^{-8} and 19.6 kJ mol^{-1} found for the isotropic process in compounds **1b**.

Raising the temperature to 335 K brings on a first-order phase transition to a cubic crystalline phase with $a = 6.8$ Å. This shows a single peak in its Mössbauer spectrum indicating rapid isotropic reorientation.

Conclusion

In this the third paper dealing with the ways in which Mössbauer spectroscopy may be used to detect rotational disorder in organometallic salts, the major advance has been the direct correlation between disorder as detected by X-ray methods and the Mössbauer spectral data. There are other examples where this correlation has been demonstrated[12] and it seems a useful direction to follow.

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