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A Mössbauer Spectroscopic Study of $[(\eta^5\text{-}C_5H_5)_2Fe]^+[(NC)_2C{=}C(CN)O]^- \cdot [(\eta^5\text{-}C_5H_5)_2Fe]_{1/2}$

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Abstract

No evidence for thermal intervalence electron transfer was found on Mössbauer spectra recorded over the temperature range 80–345 K. This indicates that any thermal intervalence transfer is less than 10^7 s^{-1}. There is an indication of disorder of the ferrocenium ions at 80 K from the Mössbauer spectrum, this point is discussed.

Introduction

Over the last three years we have reported a number of Mössbauer studies on ferrocene complexes [1–3]. The results have allowed us to show relationships between oxidation potentials and ^{57}Fe Mössbauer quadrupole splittings (QS) for a number of substituted ferrocenes. We have also been able to rationalise ferrocene and ferrocenium QS values in terms of electron donation by the ferrocenyl e_1 orbitals, and we then extended this explanation to cover previously reported Mössbauer data for biferrocenium and biferrocenylenium monocations.

In the last fourteen years a number of Mössbauer studies [4–9] on biferrocene and other complexes containing two neighbouring ferrocene moieties have been reported. Two distinct types of Mössbauer spectra have been described for the monocations of these complexes. These are (1) those that show two distinct Mössbauer sites arising from one Fe^{II} centre and one Fe^{III} centre caused where the rate of thermal intervalence transfer is less than 10^7 s^{-1} (the ^{57}Fe nuclear excited state lifetime is 10^{-7} s) in such compounds as biferrocenium triiodide [6], and (2) those that show only one Mössbauer doublet with a much reduced QS such as in biferricenylanium triiodide and related compounds [6, 7]. Here the rate of intervalence transfer due both to thermal and tunnelling processes is such that only an average iron environment is seen and hence it would be expected that the rate is greater than 10^7 s^{-1} (for detailed arguments on the apparent rate against the theoretical rate see refs. 6, 7 and 9). These latter average valence type cations have the odd electron delocalized in a molecular orbital encompassing both iron centres. The main structural difference found in the compounds that display these effects is in the Fe–Fe distances. In the case of the biferricenylenium ions it is reasonable to assume that the distance is close to that in biferrocenylene [9] (3.98 Å), whereas in compounds that show two distinct Mössbauer sites one Fe^{II} and one Fe^{III} the two Fe atoms are much further apart (around 6.0 Å [9]).

Recently a paper [10] describing the structure of $[(\eta^5\text{-}C_5H_5)_2Fe]^+[(NC)_2C{=}C(CN)O]^- \cdot [(\eta^5\text{-}C_5H_5)_2\text{-}Fe]_{1/2}$ has appeared. This material contains both ferrocene and ferrocenium ions that are not directly connected. We have undertaken a Mössbauer spectroscopic study of this material to see if the two iron sites were engaged in thermal intervalence transfer. We report the results of this study here.

Results and Discussion

$[(\eta^5\text{-}C_5H_5)_2Fe]^+[(NC)_2C{=}C(CN)O]^- \cdot [(\eta^5\text{-}C_5H_5)_2\text{-}Fe]_{1/2}$ [10] is composed of one-dimensional segregated stacks of (a) ferricenium ions and (b) alternating 1:2:1 ferrocene-bis(tricyanoethenolate)-ferrocene stacks. The latter stack can be considered as a weak 1:2 donor–acceptor complex between ferrocene and the tricyanoethanolate anion. In the ferricenium ion stack individual cations are rigorously eclipsed. The ferrocene molecules are 'ordered' and the rings are staggered. The closest approach of any two iron atoms in the structure is between the ferrocene and ferrocenium ions in adjoining stacks at the same level the Fe^{II}–Fe^{III} distance is just over 6.0 Å.

The Mössbauer spectra are presented in the Fig. 1 and the data is given in the Table I the ferrocene: ferrocenium ratio at 80 K is exactly as expected from the crystal structure (carried out at room temperature). The ratio actually found in the Mössbauer spectrum at room temperature is 70:30 ferrocenium: ferrocene, the small difference from that expected is possibly due to slight differences in the recoil free

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TABLE I. The Temperature Dependence of the ^{57}Fe Mössbauer Parameters for $[(\eta^5\text{-}C_5H_5)_2Fe]^+[(NC)_2C{=}C(CN)O]^-\cdot[(\eta^5\text{-}C_5H_5)_2Fe]_{1/2}$.

K	Ferrocene					Ferrocenium Ion				
	δ mms^{-1} [a]	Δmms^{-1}	Γmms^{-1}	Intensity	% Area	δ mms^{-1} [a]	Δmms^{-1}	Γmms^{-1}	Intensity	% Area
80	0.52(1)	2.43(2)	0.29(3)	9.3(2)	33.66(1.25)	0.52(1)	0.0	0.68(3)	15.7(2)	66.34(1.31)
298	0.41(1)	2.42(2)	0.27(2)	4.0(2)	29.58(2.81)	0.40(1)	0.0	0.38(2)	13.7(2)	70.42(2.9)
345	0.31(2)	2.46(3)	0.28(2)	3.6(3)	29.37(2.39)	0.30(1)	0.0	0.39(2)	12.3(2)	70.63(1.8)

[a] Isomer shifts relative to natural iron absorbers.

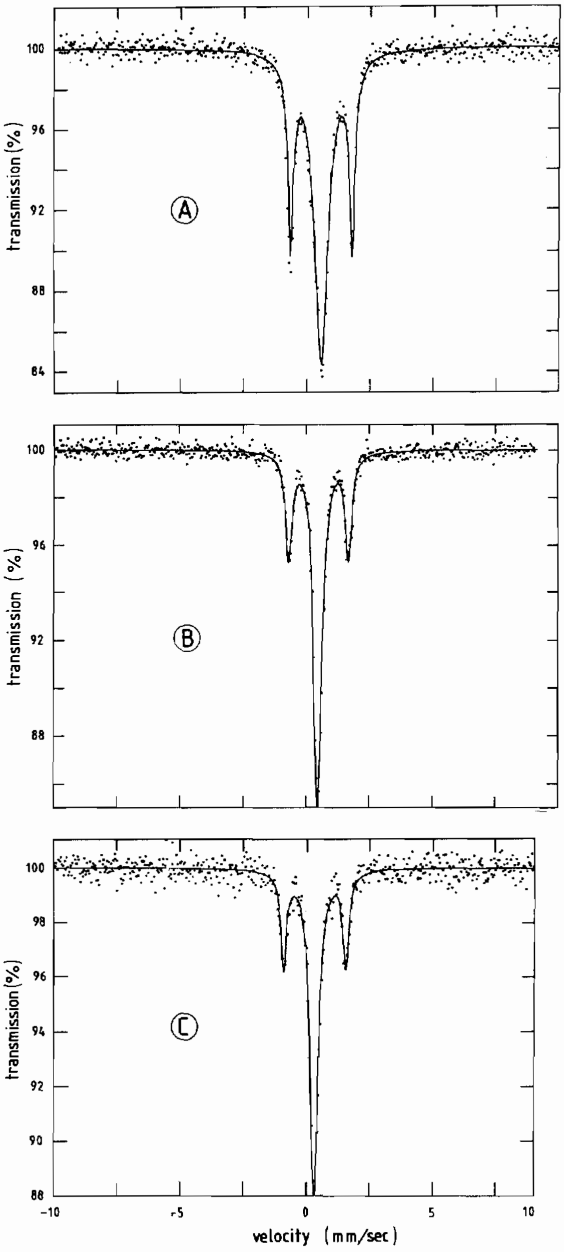

Fig. 1. ^{57}Fe Mössbauer spectra of the title complex at A = 80 K; B = 298 K; C = 345 K. The sample at 80 K was quench cooled.

fraction of the two sites. The isomer shifts and quadrupole splittings are typical for ferrocene and ferrocenium compounds; there is little obvious temperature dependence of these latter parameters and this must be interpreted as indicating that any thermal intervalence transfer is less than 10^7 s^{-1}. This result is consistent with Fe^{II}–Fe^{III} distances greater than 6.0 Å.

The unexpected feature of the Mössbauer spectra is the large line width found for the ferrocenium site at low temperature and its dramatic decrease seen for the highly ordered eclipsed ferrocenium ions at room temperature. The most probable explanation for the large line width at 80 K is that the ferrocenium ions are disordered at 80 K due to a low temperature phase change. The sharper line at room temperature just reflects the highly ordered ferrocenium sites and is not due to an 'average' site caused by motion of the molecules such as that reported for the cations in (η-cyclohexatriene)(η-cycloentadienyl)iron(II) PF_6 by Fitsimmons [11], as in our case the ferrocenium ions are said to be stationary [10].

Experimental

The complex was prepared as in ref. [9]. The Mössbauer spectrometer has been described previously [12].

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