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Interesting magnetic effects caused by bulky substituents in ferrocenium salts. Zero applied-field magnetic hyperfine interactions in 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocenium triflate

A. Houlton, R.A. Brown, J.R. Miller, R.M.G. Roberts, J. Silver
Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ (UK)

and M. Thomas
Department of Physics, University of Liverpool, Liverpool L69 3BX (UK)

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Abstract

57-iron Mössbauer spectroscopy reveals that 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocenium triflate exhibits slow paramagnetic relaxation at 80 K. Resolved magnetic hyperfine splitting is observed below 9 K. This is the first example of such behaviour for a ferrocenium salt containing a diamagnetic anion.

The predominant electronic relaxation mechanism for low-spin iron(III) complexes is spin–lattice relaxation. As this is usually fast, owing to large spin–orbit coupling, magnetic hyperfine splittings of their 57-iron Mössbauer spectra are rarely observed [1]. Interestingly, anomalous effects have been seen in compounds based on ferrocenium [2]. The $S = 1/2$ ferrocenium ion (**1**) (included here as its triflate salt) exhibits a singlet zero-field Mössbauer spectrum at all temperatures. However, decamethylferrocenium (**2**) displays a variety of behaviours, from slow paramagnetic relaxation to co-operative magnetic ordering depending on the accompanying anion and on the solid state structure [2,3]. The most obvious feature distinguishing these two cations is the increased steric bulk of the latter. These observations have prompted us to investigate other bulky ferrocenium compounds and we now report 57-iron Mössbauer data for 1,1′,3,3′-tetrakistrimethylsilylferrocinium (**3**).

Correspondence to: Dr. J. Silver, Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK.

Table 1

57-Iron Mössbauer spectroscopic parameters for **1** and **3** at various temperatures

	δ (mm s^{-1})	$\Gamma_{1/2}$ (mm s^{-1})	H (mm s^{-1})	τ (s)
1 Room temperature	0.44(1)	0.25(1)		
80 K [a]	0.53(1)	0.21(1)		
	0.54(1)	1.19(5)		
4.2 K [b]	0.57	0.16	385.7	$< 4.3 \times 10^{-9}$
1.3 K [b]	0.57	0.15	412.7	$< 4.3 \times 10^{-9}$
3 Room temperature	0.48(1)	0.20(1)		
80 K [a]	0.54	0.15		
	0.54	1.95		
4.2 K [b]	0.52	0.37	399.6	1.19×10^{-7}
	0.52	0.45	299.5	2.38×10^{-8}
1.3 K [b]	0.48	0.37	402.1	1.25×10^{-7}
	0.48	0.45	288.5	2.67×10^{-8}

[a] Spectra fitted as 2 Lorenzian lines; a narrow singlet and a broad background. [b] The relaxation fits were based on the simple two level model of Blume and Tjon [9] whereby the hyperfine field detected by the nucleus reverses in direction at a rate fixed by the fitting procedure. Isomer shifts are reported relative to natural iron at room temperature.

Table 1 presents 57-iron Mössbauer data for **1** and **3** as salts with the diamagnetic triflate anion. Compound **1** shows a singlet at room temperature with slight broadening at 80 K. A sharp resonance line is observed at lower temperatures, down to 1.3 K. This is indicative of fast relaxation ($\tau < 10^{-9}$ s) and is in keeping with other studies [4].

The data for **3** indicate more complex behaviour. Figure 1 shows the Mössbauer spectra of **3** at two temperatures. A narrow singlet is observed at room temperature but at 80 K the line is considerably broadened, indicating the slowing down of paramagnetic relaxation. Such extreme broadening at this temperature is unprecedented in ferrocenium salts. At 9 K, resolved magnetic hyperfine structure is observed. At both 4.2 and 1.3 K two components of the spectra are clearly seen, in a ratio 7:3. The corresponding relaxation times at 1.3 K for the respective components are 1.25×10^{-7} and 2.67×10^{-8} s. In (**3**) [triflate] the splitting of the major component corresponds to an effective field of ~ 37 T. While this is considerably larger than the typical 11 T/spin, such large internal fields are not unusual for ferrocenium derivatives [4,5]. It is thought that there is a considerable orbital contribution to the observed field [4,6*]. Since only spin–lattice, and not spin–spin, relaxation is temperature dependent these observations imply smaller spin–orbit coupling for **3**, and perhaps for ferrocenium compounds in general, than expected for low-spin ferric complexes [1].

Spin–spin relaxation depends on spin–spin coupling and is proportional to $\langle r^{-3} \rangle$. In the case of high-spin iron(III) complexes, iron atoms separated by ~ 9.5 Å show definite magnetic structure in their Mössbauer spectra in contrast to those at ~ 6 Å separation [1]. Similar effects are apparent in ferrocenium structures. As a single crystal X-ray structure study of **3** was thwarted by the repeated failure of

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* Reference number with asterisk indicates a note in the list of references.

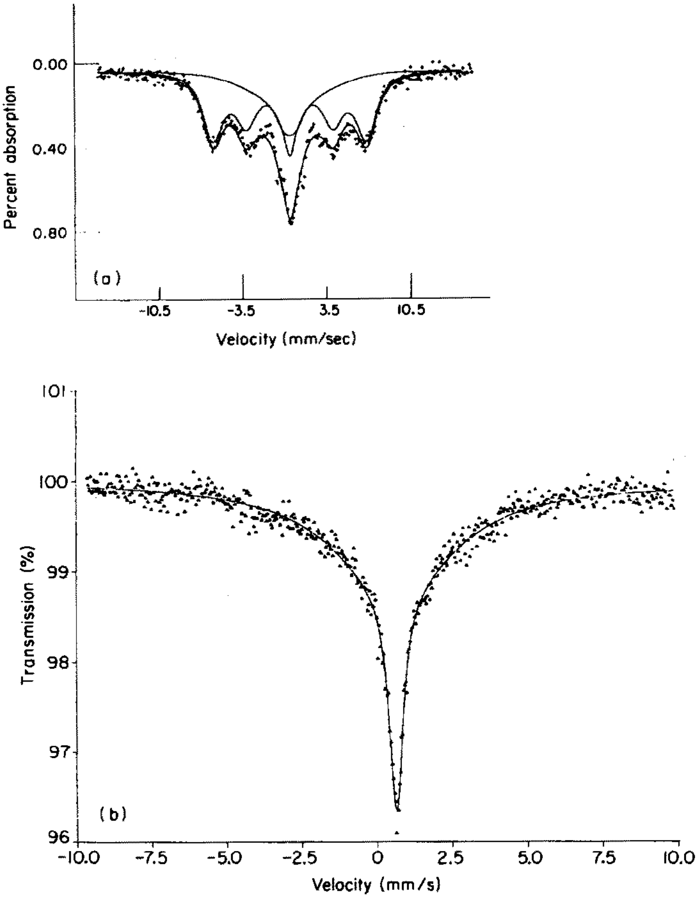

Fig. 1. Mössbauer spectra of 3 at (a) 1.3 K and (b) 80 K. See Table 1 for fitting details.

attempts to prepare suitable crystals, Fe · · · Fe distances are unknown. However, an indication can be gained from the structure of the unoxidized parent ferrocenyl derivative [7], in which the shortest Fe · · · Fe separation is 7.33 Å. This is clearly long compared to such distances in the structures of 1, with various anions, which range from 5.83–6.89 Å [8*]. In the case of 2, distances are more typically ~ 8.5 Å, though some shorter distances, ~ 7.9 Å, are observed [8*]. Obviously, the steric bulk of the substituent groups in 2 and 3 causes these larger Fe · · · Fe separations which in turn lead to a decrease in the spin–spin relaxation rate. The presence of two components in the spectra of 3 below 4.2 K dictates that two unique iron environments exist, distinguished by the distances of surrounding iron centres thus giving rise to differing relaxation rates.

When the anion is replaced with the paramagnetic $[FeCl_4]^-$ ion no spectral broadening is apparent in the 80 K spectrum. On first consideration this might be thought to be due to an increase in the spin–spin relaxation rate, arising from a decrease in the Fe · · · Fe distances. However, this cannot be the case as spin–spin relaxation necessitates a conservation of spin populations and hence only like spins can participate in such a process. The incorporation of $[FeCl_4]^-$ must increase the ferrocenium relaxation rate through a spin–lattice relaxation mechanism.

In conclusion, ferroceniums comprise a class of low-spin iron(III) complexes that can display interesting magnetic effects. In these systems the spin-lattice relaxation rate is not always sufficient to enable rapid relaxation of the ferrocenium spins (*i.e.* $< 10^{-9}$ s) at all temperatures. In the case of diamagnetic anions, when the Fe $\cdots$ Fe separations are not too great, $\sim < 7$ Å, spin–spin relaxation can contribute to maintaining fast relaxation as temperatures decrease. Where the distances are longer this contribution can become insufficient and magnetic hyperfine splittings are observed.

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