Valence-detrapping Modes and Phase Transitions affecting the Intramolecular Electron-transfer Rate of Mixed-valence Biferrocenium Cation

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The results of an *X*-ray structure determination of biferrocenium tri-iodide, the dramatic effects of changing from the tri-iodide to the bromoiodide anion upon the temperature of conversion from two Mössbauer doublets to one, and an endothermic differential scanning calorimetry peak at 335 K for biferrocenium tri-iodide indicate that it is lattice dynamics that control the intramolecular electron transfer in mixed-valence biferrocenes.

Taube[1] and Cowan[2] pioneered the use of mixed-valence transition metal complexes to probe electron transfer between well separated metal sites. In spite of considerable work in this area,[3] however, the detailed mechanism of *intra*molecular electron transfer in a mixed-valence complex is not very well known. In this communication it will be shown that changing the counterion from I_3^- to Br_2I^- has a profound effect on the rate of intramolecular electron transfer in the mixed-valence biferrocenium cation. This fact together with other data presented in this report indicate that the rate of *intra*molecular electron transfer for many mixed-valence complexes in the solid state is controlled by lattice dynamics.

The molecular and solid-state structure of biferrocenium tri-iodide (**1**) has been determined at 296 K by single-crystal *X*-ray diffraction techniques.† As can be seen in Figure 1, the mixed-valence biferrocenium cation has a *trans*-conformation; the two iron ions in the cation are on opposite sides of the planar fulvenide ligand. The angle between the two rings of each $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$ moiety is 0.3(3)°. Furthermore, the two rings are eclipsed. The mixed-valence cation sits on a centre of symmetry with an Fe-to-ring centroid distance, 1.681(4) Å, for each metallocene moiety that is intermediate between that in Fe^{II}, 1.66 Å,[4] and Fe^{III}, 1.70 Å,[5] metallocenes. As viewed down the *b*-axis the solid-state structure of (**1**) is dominated by segregated columns of biferrocenium cations and tri-iodide ions, where each column of I_3^- anions is surrounded by four columns of cations. As is evident in Figure 2, it is also possible to describe the packing arrangement in (**1**) as step-like stacks of biferrocenium cations developing approximately along a body-diagonal of the unit cell.

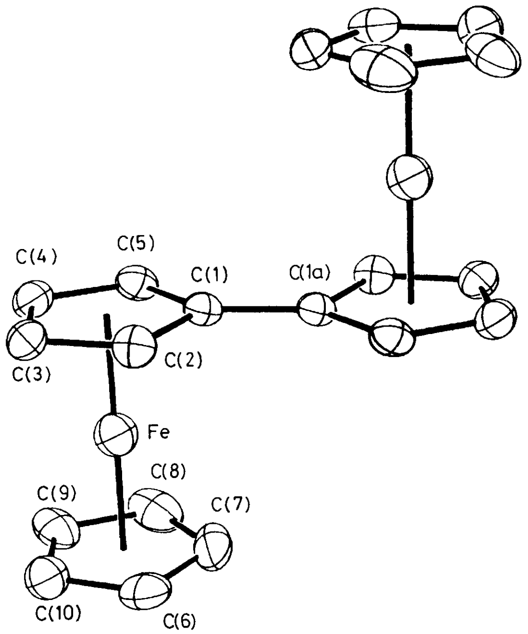

Figure 1. ORTEP plot of the biferrocenium cation in (**1**). Atoms are shown as 50% equiprobability ellipsoids.

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† *Crystal data* for (**1**): $C_{20}H_{18}Fe_2I_3$, $M = 750.7$, triclinic, space group $P\bar{1}$, $a = 7.5779(20)$, $b = 8.4742(14)$, $c = 9.5577(21)$ Å, $\alpha = 112.619(14)°$, $\beta = 104.646(20)°$, $\gamma = 94.610(19)°$, $U = 537.20(19)$ Å^3, $Z = 1$, $D_c = 2.32$ g/cm^3, $F(000) = 351$. Data were collected at 23 °C on a Nicolet R3 automated diffractometer *via* an ω-scan procedure and were corrected for absorption ($\mu = 56.19$ cm^{-1}, Mo-K_α). Of 2580 reflections collected ($4° < 2\theta < 55°$), 2435 were unique, and of these 2185 that were considered observed [$F_o > 2.5\sigma(F_o)$] were used in the solution (intuitive: $Z = 1$, therefore, half-occupancy I atom at 0,0,0) and refinement (blocked cascade). All hydrogen atoms were located and isotropically refined; non-hydrogen atoms anisotropically. $R_F = 0.036$, $R_{wF} = 0.042$, goodness-of-fit = 1.20.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

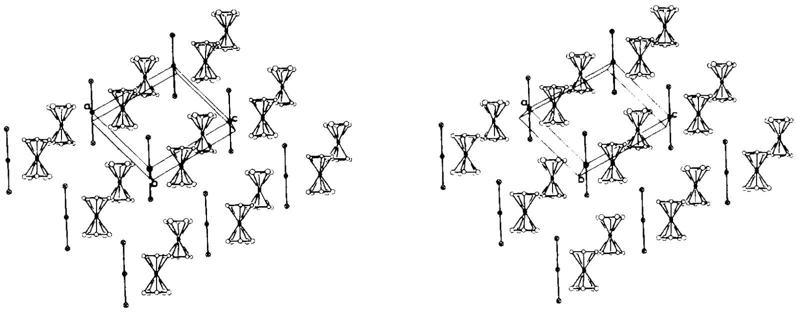

Figure 2. Stereoview of the packing arrangement of biferrocenium tri-iodie, (**1**), as viewed down the *b*-axis.

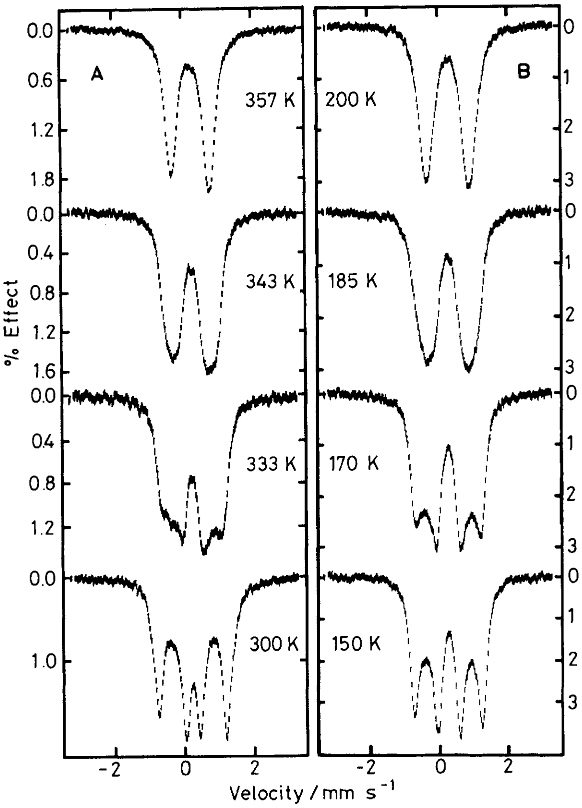

Figure 3. Variable-temperature ^{57}Fe Mössbauer spectra for: (A) biferrocenium tri-iodide (**1**); (B) biferrocenium dibromoiodide (**2**).

In agreement with previous work[6] we find that samples of (**1**) at 298 K give a Mössbauer spectrum with two quadrupole-split doublets, one characteristic of a Fe$^{\text{II}}$ metallocene and the other a Fe$^{\text{III}}$ metallocene. A few diffusion-recrystallized samples of (**1**) were found to give a Mössbauer spectrum with up to ~35% of the spectral area in the form of a single 'valence-delocalized' doublet. As can be seen in Figure 3, an increase in the temperature of (**1**) leads eventually to a change in the spectrum such that only a single 'average-valence' doublet is seen above ~350 K. The apparent inconsistency between the above *X*-ray structure at 296 K which indicates a centrosymmetric structure for the mixed-valence cation and the 298 K Mössbauer spectrum with two doublets can be resolved most easily by assuming that the crystal structure is an artefact of a static disorder of 'valence-localized' cations. Large thermal parameters on the atoms of the I_3^- anion are consistent with this interpretation.

An unusual result obtains when the I_3^- anion of (**1**) is replaced by the (Br–I–Br)$^-$ anion to give compound (**2**). This biferrocenium salt shows localized behaviour at temperatures below ~150 K (see Figure 3), but increasing the temperature of (**2**) up to ~200 K gives a spectrum with but one 'valence-delocalized' doublet. The change from I_3^- in (**1**) to Br_2I^- in (**2**) leads to a change of ~150 K in the temperature at which the mixed-valence biferrocenium ion transfers electrons faster than the Mössbauer time-scale (*i.e.*, faster than ~10^7 s^{-1}).

The above observations of pronounced counterion dependence of electron-transfer rate and the nature of the temperature dependence of the Mössbauer spectra reported[7] for 1′,6′-diethylbiferrocenium tri-iodide and 1′,6′-dipropylbiferrocenium tri-iodide can be explained by the presence of an order–disorder phase transition. That is, at low temperature the biferrocenium cations are valence localized, which would require that each anion be disposed such that it is closer to the Fe$^{\text{III}}$ site of neighbouring cations. This 'local distortion' would be ordered in domains (homogeneous regions in the crystal) if there is an appreciable interaction between molecules. As the temperature of a given crystallite is increased, disorder would set in at some temperature. This would simply mean that for random cations the odd electron would transfer from the Fe$^{\text{II}}$ to the Fe$^{\text{III}}$ ion and the neighbouring anion(s) would also adjust its position. Further increase in the temperature would eventually lead to very rapid *intra*molecular electron transfer in all the cations. The anions would be jumping between two positions in the lattice at some phonon frequency. The phonons excited at the phase transitions are the valence-detrapping modes in the solid state. It must be emphasized that the temperature dependence seen in the Mössbauer spectra of (**1**), (**2**), and analogous mixed-valence complexes is due to lattice dynamics and does not directly reflect *intra*molecular electron transfer. This explains why the Br_2I^- salt experiences a transformation to valence delocalized behaviour at lower temperatures, for the shorter Br_2I^- anion is of lower mass than the I_3^- anion and the phonon mode involving the Br_2I^- anion would be at lower energy.

The presence of phase transitions in (**1**) is conclusively indicated by differential scanning calorimetry carried out between ~150 and ~370 K. An endothermic peak is seen at ~335 K. Furthermore, we find that for certain mixed-valence biferrocenes, such as 1′,6′-dibenzylbiferrocenium tri-iodide (**3**), the level of crystallinity of the compound dramatically affects the appearance of the Mössbauer spectrum. Microcrystalline (**3**) gives a spectrum with two doublets (*i.e.*, valence localized) at 298 K, whereas, a diffusion-recrystallized form of (**3**) at 298 K gives a single doublet which is characteristic of a 'valence-delocalized' species. The level of defect structure can vary from a microcrystalline to a crystalline sample and this can dramatically affect a co-operative phase transition.[8]

It is likely that lattice dynamics generally control the rate of *intra*molecular electron transfer for many mixed-valence complexes. In a recent communication[9] an oxo-centred mixed-valence trinuclear iron complex was shown to undergo in the solid state a transformation from statically disordered at low temperatures to dynamically disordered which controlled the rate of *intra*molecular electron transfer.

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