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Preliminary Communication

Syntheses and structures of decamethylbiferrocene mono- and di-cation triiodides

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Abstract

The mono- and di-cations of decamethylbiferrocene (**1**) have been obtained as triiodide salts by oxidation of decamethylbiferrocene with I_2 in THF. The X-ray crystal structure of [**1**](I_3) at 295 K and the Mössbauer data show a localized mixed-valence system. The salt [**1**]$(I_3)_2$ has a single Mössbauer quadrupole doublet at 4.5 K with Fe^{III} parameters (IS = 0.537 mm s^{-1} *vs.* Fe; QS = 0.237 mm s^{-1}) with small antiferromagnetic coupling ($\theta = -5.58$ K).

The chemistry and physics of biferrocene derivatives first attracted attention more than two decades ago [1,2]. There is now a revival of interest since the discovery of the ferromagnetic properties of decamethylferrocenium salts [3] and because of the search for systems designed as molecular electronic devices [4]. The examination of the electrical communication between two metal centres via a hydrocarbon bridge is a challenging aspect of the latter area.

With our research interest in hydrocarbon-bridged bimetallic systems [5], we recently reported the first syntheses of decamethylbimetallocenes, including biferrocenium hexafluorophosphate [**1**][PF_6] [5]. This exhibits valence localization on Mössbauer and infrared time scales [5–7]. In view of the dramatic influence of the counter anion on electron localization in biferrocenium salts in the solid state [8,9], we have now synthesized the triiodide salts in the mono- and di-oxidized series. The first X-ray crystal structure of a decamethylbimetallocene cation is reported, as well as preliminary data for [**1**]$(I_3)_2$.

[**1**](I_3) [5] is obtained by dropwise addition of 1.5 equivalents of I_2 in THF to a solution of the neutral complex in a mixture Et_2O/THF (80/20). Recrystallization from a saturated CH_3CN solution at −20°C gave an 86% yield of blue crystals suitable for crystallographic determination. This complex crystallizes in the space group $P\bar{1}$ with $Z = 2$ (Table 1 *). A perspective

TABLE 1. Crystal data and data collection parameters of [**1**](I_3)

Formula	$C_{30}H_{38}Fe_2I_3$
F.W., g mol^{-1}	891.04
System	triclinic
Space group	$P\bar{1}$
a, Å	12.043(3)
b, Å	12.016(2)
c, Å	12.101(3)
α, °	90.75(1)
β, °	89.85(2)
γ, °	116.20(2)
V, Å^3	1571
Z	2
μ(Mo Kα), cm^{-1}	38.58
ρ_{calc}, g cm^{-3}	1.88
2θ range, °	$2 \leq 2\theta \leq 52$
Scan type	$\omega/2\theta$
Scan width, °	$0.8 + 0.345 tg\theta$
Scan speed, ° min^{-1}	$1.8 \leq$ s.p. ≤ 20.1
No. of reflctns. collected	6462
No. of unique reflctns.	6152
No. of reflctns with $I \geq 3\sigma(I)$	4770
Decay (%)	< 1
No. of variables refined	317
R [a]	0.054
R_w [b]	0.065
Weighting scheme	$w = 1$

[a] $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$.

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Any request should be accompanied by the full literature citation communication.

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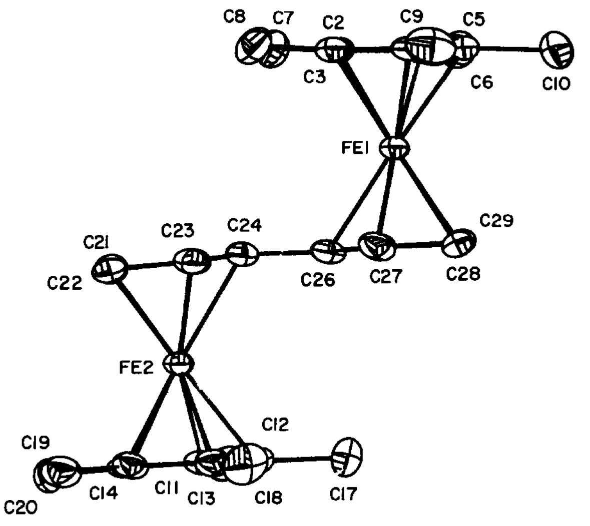


Fig. 1. ORTEP drawing of the decamethylbiferrocenium salt [1](I$_3$) at 295 K.

drawing of the cation is shown in Fig. 1 as well as a packing arrangement in Fig. 2. The two metallocene moieties are dimensionally inequivalent. Distances from the iron atoms to the least-squares mean planes of the two C_5Me_5 rings are 1.669 Å and 1.712 Å, those from the iron atoms to the C_5H_4-rings are 1.651 Å and 1.697 Å. These are significantly different, indicating two distinct oxidation states for the iron in the dimer. This is a rare case of an electron-localized mixed valence complex [9c]. The bond distances within the asymmetric I_3^- counterion are 2.880(1) Å and 2.933(1) Å. The shortest Fe $\cdots$ I distance of 5.078(2) Å is that between the Fe^{III} and the iodine atom which probably carries the greater negative charge. This distance is similar to that found in di-n-butylbiferrocenium triiodide at 150 K.

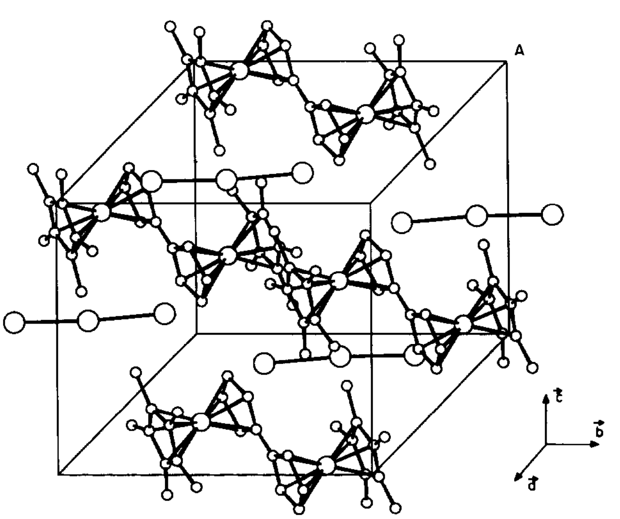
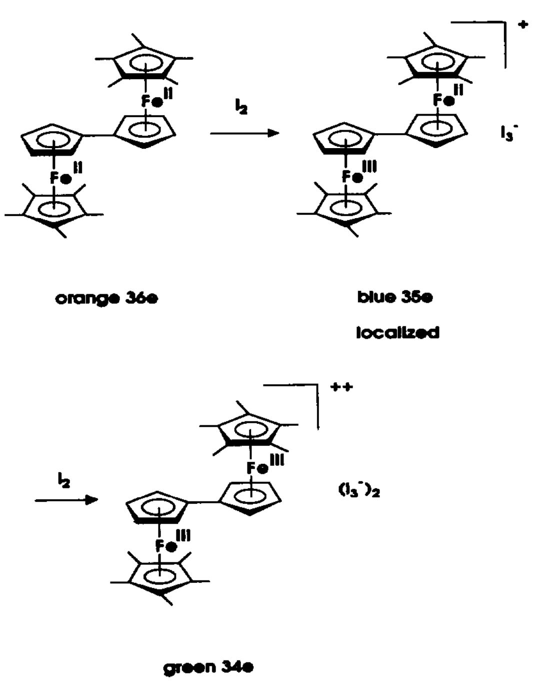


Fig. 2. Stereoview of the packing arrangement of compound [1](I$_3$) at 295 K.



The Mössbauer parameters are similar to those of the PF_6^- salt: IS = 0.512(1) mm s^{-1} (*vs.* iron metal at room temperature) QS = 2.143(2) mm s^{-1} for Fe^{II}; IS = 0.514(2) mm s^{-1} (*vs.* iron metal at room temperature) QS = 0.396(3) mm s^{-1} for Fe^{III}. They indicate a localized mixed valence on the time scale of the technique (10^{-7}–10^{-9}s^{-1}) at all temperatures down to 4.2 K.

The dioxidized species [10] was synthesized using 6 equivalents of I_2 added to a THF solution of 1. The mixture was stirred overnight, filtered and the product recrystallized from CH_3CN solution giving a 74% yield of the dark-green salt. The Mössbauer spectra [1](I$_3$)$_2$

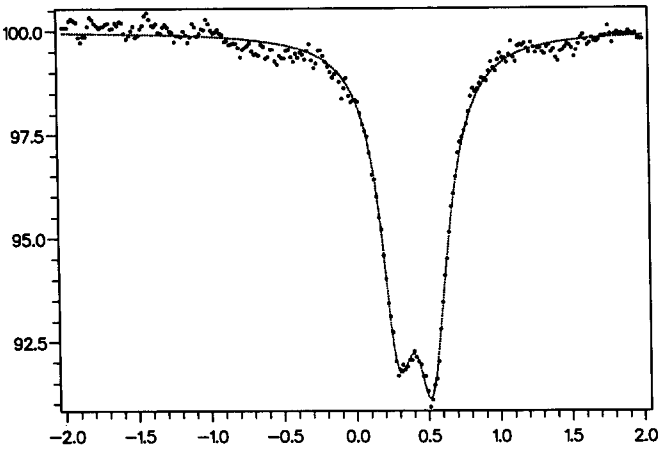


Fig. 3. Mössbauer spectrum of [1](I$_3$)$_2$ at 4.5 K.

obtained at 4.5, 15, 30, 50, 77, 120, 200, and 300 K (Fig. 3) display an unusual thermal dependence. Below 15 K they consist of a single quadrupole doublet with hyperfine parameters typical of Fe^{III} (IS = 0.537(2) mm s^{-1} *vs.* iron metal at room temperature, QS = 0.237(2) mm s^{-1}). On increasing the temperature, the line shape progressively evolves with Lorentzian broadenings typical of a slow relaxation of the magnetic hyperfine interaction. However, in this case, the broadenings correspond to a relaxation rate which decreases with increasing temperature. Large antiferromagnetic interaction is excluded by magnetic measurements which show an $S = 0$ ground state with $\theta = -5.58$ K for $[1](I_3)_2$.

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10 $[1](I_3)_2$: Anal. Calcd for $C_{30}H_{38}Fe_2I_6$: C, 28.33; H, 3.01; Fe, 8.78. Found: C, 28.25; H, 2.97; Fe, 8.94. IR (KBr pellet, ν cm^{-1}): 847 δ(CH).