Mössbauer and Magnetic Susceptibility Studies of Biferrocenylene(II,III) Picrate

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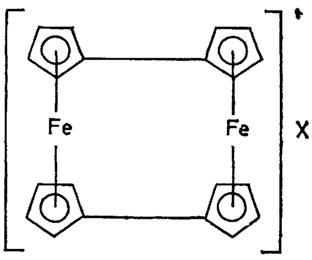
Summary Mössbauer and magnetic susceptibility studies of biferrocenylene(II,III) picrate show that extensive donor–acceptor interactions occur in this mixed-valence molecule which result in fractional oxidation states for the iron atoms.

WE recently described[1] the synthesis and spectral properties of mixed-valence salts of biferrocenylene (**1**) (bisfulvalenedi-iron, BFD). We now report the results of Mössbauer and magnetic susceptibility studies of (**1a**) which bear upon the question of the ground-state electronic configuration of the biferrocenylene monocation.

The characteristic differences in the quadrupole splitting parameters (Q.S.) for ferrocene (2·4 mm s^{-1}) and ferrocenium ion (0—0·8 mm s^{-1})[2] are particularly useful in defining the 3*d* configuration of the iron atom. In this way, biferrocene(II,III) picrate was shown to have trapped valences,[3] as its Mössbauer spectrum is a composite of ferrocene (2·14 mm s^{-1}) and ferrocenium (0·288 mm s^{-1}) transitions.

In contrast to this, the Mössbauer spectra of (**1a**) at 77 and 298 K show only two lines, indicating that only one type of iron is present. The quadrupole splitting parameter is 1·78 mm s^{-1}, intermediate between that for ferrocene and ferrocenium ion. [(**1a**) (298 K), Q.S. = 1·75 mm s^{-1}, isomer shift relative to iron foil (I.S.) = 0·436 mm s^{-1}; (**1a**) (77 K) Q.S. = 1·78 mm s^{-1}, I.S. = 0·525 mm s^{-1}; biferrocenylene (298 K), Q.S. = 2·44 mm s^{-1}, I.S. = 0·455 mm s^{-1}: biferrocenylene (77 K), Q.S. = 2·46 mm s^{-1}, I.S. = 0·535 mm s^{-1}: uncertainties are less than 0·01 mm s^{-1}; all line widths are about 0·3 mm s^{-1} (FWHM)]. The presence of only one type of iron could arise from either oscillation of valence at a rate greater than 10^8 s^{-1}, or delocalization of the odd electron through either metal–metal or metal–ligand–metal interaction, in which case, fractional valency must be ascribed to this system. The sites, however, are not exactly equivalent. There is an asymmetry in the intensity of the two Mössbauer lines which is stronger in the room-temperature spectrum. This slight difference in iron sites may reflect a distortion due to the picrate ion, or perhaps a Jahn–Teller effect. To clarify this point, we are presently investigating biferrocenylene(II,III) tetrafluoroborate (**1b**).



(1) a; X = picrate
b; X = BF_4^-

FIGURE

There is corroborative evidence for the presence of only one type of iron from preliminary ESCA measurements which show only one $Fe^2P_{3/2}$ transition with a half-width of 1·5—1·8 eV.† This is to be contrasted with the two lines observed for biferrocene [$Fe^{II}Fe^{III}$] picrate.[4]

The magnetic susceptibility of (**1a**) was determined in the range 2—300 K by a modified Faraday method.[5] The measured susceptibility, corrected for diamagnetism, follows a Curie law and can be expressed by $\chi = (0{\cdot}372/T$

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† We thank Mr. M. Mertes for obtaining these measurements for us.

$+ 250 \times 10^{-6}$) $cm^3 \, mol^{-1}$. The spin-only value of the Curie constant is $\chi(T) = C = N\beta^2 g^2 S \, (S + 1)/3k = 0{\cdot}375$ cm^3 K/mol for $S = 1/2$ and $g = 2$.

The room-temperature magnetic moment, calculated by $\mu_{eff} = 2{\cdot}828 \, (\chi T)^{1/2}$, is 1·88 B.M., which is in close agreement with the spin-only value of 1·73 B.M. This is in contrast to other ferrocenium and dicarbollide complexes,[6] including biferrocene(II,III) picrate,[7] whose room-temperature moments range from 2·3 to 2·6 B.M., characterizing an $^2E_{2g}[(a_{1g})^2(e_{2g})^3]$ ground state. The disparity between these values and that found for (**1a**) indicates that the monocationic salts of biferrocenylene cannot be treated simply as substituted ferrocenium salts, but rather that extensive interactions occur which alter the 3*d* configuration of the iron atoms.

The Mössbauer, magnetic susceptibility, and ESCA measurements all suggest that biferrocenylene picrate is fractionally valent. This contradicts our previous suggestion[1a] that the compound showed trapped valence behaviour on the basis of the intensity of the near-i.r. transition ($\alpha < 0{\cdot}25$).‡

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‡ The equation used to calculate the interaction parameter (α) is valid only when there is weak interaction. Biferrocene [$Fe^{II}Fe^{III}$] picrate satisfies this condition but compound (**1a**) does not.

[1] (a) D. O. Cowan and C. LeVanda, *J. Amer. Chem. Soc.*, 1972, **94**, 9271; (b) U. T. Mueller-Westerhoff and P. Eilbracht, *ibid.*, p. 9272.
[2] R. L. Collins and R. Pettit, *J. Inorg. Nuclear Chem.*, 1967, **29**, 503.
[3] D. O. Cowan, R. L. Collins, and F. Kaufman, *J. Phys. Chem.*, 1971, **75**, 2025.
[4] D. O. Cowan, J. Park, M. Barber, and P. Swift, *Chem. Comm.*, 1971, 1444.
[5] G. A. Candela and R. E. Mundy, *Rev. Sci. Instr.*, 1965, **36**, 338.
[6] D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, *Inorg. Chem.*, 1971, **10**, 1559.
[7] D. O. Cowan, G. A. Candela, and F. Kaufman, *J. Amer. Chem. Soc.*, 1971, **93**, 3889.