Synthesis and Complex Formation of Diferrocenyltetrathiafulvalene

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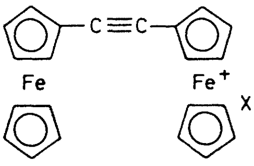
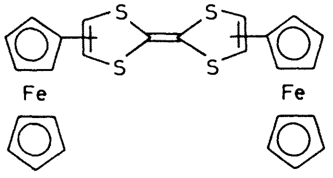
Summary Diferrocenyltetrathiafulvalene (**2**) contains two electron donor sites, the tetrathiafulvalene and ferrocene units; its charge transfer complexes with acceptor molecules such as tetracyanoquinodimethane (TCNQ) or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) have been isolated.

THERE has recently been great interest in the 1 : 1 complex of tetrathiafulvalene (TTF) with TCNQ because of its unusual electrical and magnetic properties.[1] Mixed-valence compounds such as (**1**) also exhibit unique electrical properties owing to a rapid electron exchange between Fe^{II} and Fe^{III}.[2] In connection with our studies on TTF derivatives,[3] we report here the preparation of 4,5(5′)-diferrocenyltetrathiafulvalene (**2**) and its behaviour as a new donor molecule. Compound (**2**) is particularly interesting, for it possesses two electron donor sites, the TTF and ferrocene units.

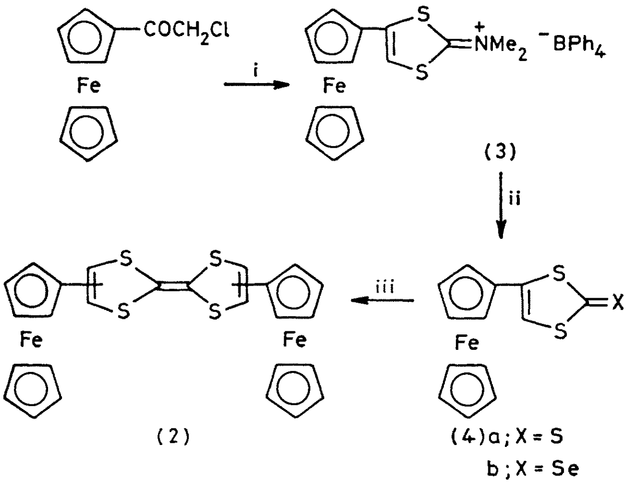


(1)



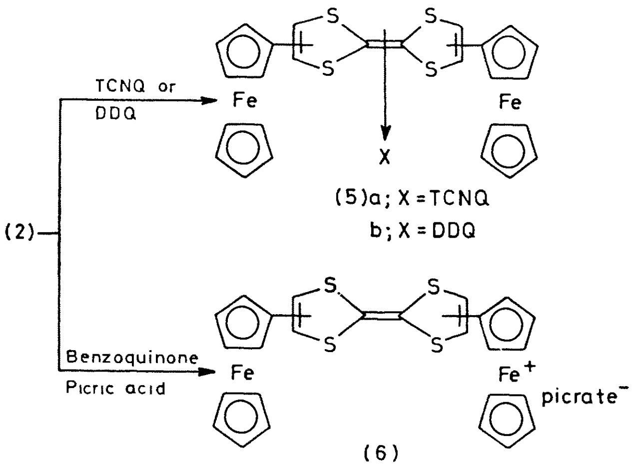
(2)

The synthetic sequence is summarized in the Scheme.† *NN*-Dimethyl-4-ferrocenyl-1,3-dithiol-2-iminium tetraphenylborate (**3**) prepared in 63% yield by the usual cyclization method[4] starting from chloroacetylferrocene,[5] was converted into the corresponding thione (**4a**) (92% yield) and selenone (**4b**) (71% yield) with sodium hydrogensulphide in dimethylformamide–acetic acid, and sodium hydrogenselenide in ethanol, respectively; (**4a**), m.p. 142—145 °C, ν C=S 1060 cm^{-1}; (**4b**), m.p. 156·5—158 °C, ν C=Se 950 cm^{-1}.



SCHEME. i, NaSCSNMe$_2$, H$_2$SO$_4$–NaBPh$_4$; ii, NaSH or NaSeH; iii, (EtO)$_3$P.

After several attempts, it was found that coupling of the selenone (**4b**) was effected by refluxing for 6 h with an excess of triethyl phosphite in benzene solution resulting in the formation of diferrocenyltetrathiafulvalene (31% yield) without decomposition of the ferrocene nucleus: (**2**), m.p. > 300 °C, *m/e* (M^+) 572, 507, 452, 318, 274, 210, 185, 177, 152, 121, 65, and 55.‡



The donor property of (**2**) was demonstrated by the successful formation of charge transfer complexes with TCNQ and DDQ in methylene chloride at room temperature. Both (**5a**) and (**5b**) were found to be 1 : 1 complexes§ and were obtained as blackish green solids. Oxidation of (**2**) with benzoquinone in the presence of picric acid in benzene solution at room temperature afforded the picrate (**6**).

The electronic spectra of the complexes (**5a**) and (**5b**) and the picrate salt (**6**) are summarized in the Table. These data suggest that the salt (**6**) is ferrocenium picrate rather than a tetrathiafulvalenium ion, since the observed spectrum of (**6**) is similar to that of the simple ferrocenium picrate.[6]

TABLE. Electronic spectral data for (**5a**), (**5b**), and (**6**)[a] (λ/nm)

(**5a**)	395, 680 743, 840
(**5b**)	348, 463, 542, 593, 680
(**6**)	380, 617,
Ferrocenium picrate[b]	375, 617

[a] Spectra were recorded in acetonitrile. [b] See ref. 6.

On the other hand, the DDQ complex (**5b**), which has a specific electrical resistivity of 855 Ω cm at room temperature,¶ is assumed to be mainly the tetrathiafulvalenium ion because the electronic absorptions, except for one at 680 nm,

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† All new compounds obtained had satisfactory spectral data and elemental analyses.

‡ Compound (**2**) was purified by recrystallization from chloroform and might be a mixture of two positional isomers. No attempt was made to separate a single isomer.

§ The ratios of the complexes (**5a**) and (**5b**), and the salt (**6**) were determined by elemental analyses.

¶ Resistivity in Ω cm for 2 probe, room-temperature compaction, between hardened steel pistons, at a pressure of 500 kg cm^{-2}.

correspond well to those of DDQ^{-}.[7] Therefore, the longest wavelength absorption of the diferrocenyltetrathiafulvalene cation radical might be estimated to appear at 680 nm. This value is close to that of the diphenyltetrathiafulvalene cation radical at 688 nm.[7]

Similarly, the TCNQ complex (**5a**) showed the absorption due to the TCNQ anion radical but not the absorption of the ferrocenium ion at *ca.* 617 nm indicating at least partial electron transfer from TTF to TCNQ. It is interesting to note that the ambident electron donor sites observed in the oxidation of diferrocenyltetrathiafulvalene (**2**) depended on the electron acceptor molecules.

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