Synthesis, Crystal Structure and Properties of Novel Ferrocenyl Multisulfur Compounds†

Stephen B. Wilkes,[a] Ian R. Butler,[a] Allan E. Underhill,[a] Michael B. Hursthouse,[b] David E. Hibbs[b] and K. M. Abdul Malik[b]
[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*
[b] *School of Chemistry and Applied Chemistry, University of Wales, Cardiff, PO Box 912, Cardiff CF1 3TB, UK*

Novel compounds and metal complexes containing both ferrocene and sulfur-based ligands have been prepared and their properties investigated. The reaction of $[NEt_4]_2[Zn(C_3S_5)_2]$ with (chloromethyl)ferrocene led to the compound 4,5-bis(ferrocenylmethylsulfanyl)-1,3-dithiole-2-thione. Similarly, the reaction of the salt $Cs_2[C_3OS_4]$, led to the ketone analogue, 4,5-bis(ferrocenylmethylsulfanyl)-1,3-dithiole-2-one. The latter has been used to prepare a monoanionic tetraferrocenyl nickel dithiolene complex which shows an intense NIR absorption at 1250 nm recorded in CH_2Cl_2. Intermolecular coupling of the thione gave the novel tetra(ferrocenylmethylsulfanyl)tetrathiafulvalene electrochemical investigations of which revealed characteristic ttf and ferrocenyl redox processes. The single-crystal structure of this compound has also been determined.

The design and development of new materials with the potential to operate at the molecular level has recently become a burgeoning topic within the physical sciences and chemistry in particular. Examples of various devices and components are liquid crystals,[1] molecular ferromagnets,[2] non-linear optical (NLO) materials[3] and molecular conductors.[4] Complex metal anions of sulfur-donor ligands and planar organic donor molecules derived from the ttf [tetrathiafulvalene, 2-(1,3-dithiol-2-ylidene)-1,3-dithiole] unit have been extensively studied because of their capacity to form molecular metals and superconductors[5] and more recently because of their potential applications as third-order NLO materials.[6-8]

In the past few years a number of studies have also highlighted the use of ferrocene-containing molecules within certain areas of molecular electronics. The extensive substituent chemistry of ferrocenes combined with the high versatility of the Fe^{II}–Fe^{III} redox couple of substituted ferrocenyl derivatives has led to the recognition that ferrocene may be a useful synthon in device applications, for example in molecular sensors,[9,10] NLO materials,[11-14] molecular switches[15] and molecular magnetic materials.[16]

The possibility exists to combine together within a single molecular unit the chemistry of ferrocenes and that of sulfur-based ligands. As yet virtually unexplored, research in this area offers a new perspective with which to investigate the unusual solid-state phenomena exhibited by molecular materials. Mueller-Westerhoff *et al.*[17] have prepared a tetraferrocenyl metal dithiolene complex which shows an intense electronic transition in the 1.3 μm region of the near-IR. This highlights the potential use of ferrocenyl metal dithiolenes in the design of NIR materials, *e.g.* dyes and lasers which utilise 1.3 and 1.5 μm radiation[18] as well as in the construction of NLO materials exhibiting enhanced second- and third-order properties.[11-14] A few compounds incorporating the organic donor unit of ttf with a second redox-active centre such as ferrocene have also been reported.[19-21] The addition of ferrocene as an extra electron-donor site onto the ttf moiety might not only serve to enhance its potential as an organic-based conductor but be of considerable interest within the expanding areas of supramolecular chemistry.[15]

Towards these objectives, we recently reported the synthesis and properties of the first diferrocenyl metal dithiolene complex,[22] which is similar to the Mueller-Westerhoff complex but with two instead of four ferrocene units attached to the metal bis(dithiolene) core. The work described in this paper concerns the synthesis and evaluation of several new types of molecular materials which contain two redox-active centres, one based on ferrocenes and the other on metal bis(dithiolene) and ttf-based organic donor molecules.

Experimental

Solvent and Reagent Pretreatment.—Where necessary solvents were purified by distillation prior to use. Dichloromethane was distilled from P_2O_5, ethanol over magnesium and then stored over 4 Å molecular sieves under argon prior to use.

Ferrocene carbaldehyde was obtained from Aldrich Chemical. 1-Ferrocenylmethanol,[23] $[NEt_4]_2[Zn(C_3S_5)_2]$[24] and $Cs_2[C_3OS_4]$[25] were prepared according to the literature procedures.

Instrumental Methods.—Melting points were determined using a Linkam hotstage (model TH600) with a heating rate of 3 °C min^{-1}, in conjuction with an Olympus optical microscope (model BH2) fitted with polarising filters. Infrared spectra were recorded as chloroform or dichloromethane solutions on a Perkin-Elmer 1600 series instrument, NMR spectra in deuteriochloroform on a Bruker AC-250 or SRC WH-400 spectrometer (δ in ppm relative to tetramethylsilane as internal standard), fast atom bombardment (FAB) mass spectra on a VG Analytical ZAB-E spectrometer using chemical ionisation (with ammonia as the reagent gas) and ultraviolet–visible and near-infrared spectra on a Philips Analytical PU8800 and a Beckman DK-2A ratio-recording spectrophotometer respectively. All elemental analyses were carried out using a Carlo Erba 1106 microanalyser.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Electrochemical Measurements.—The electrochemical properties of the new compounds were measured using cyclic voltammetry (CV). All CV measurements were carried out at room temperature in an electrochemical cell (volume 20 cm^3) fitted with a gold working electrode, a platinum-spade counter electrode, a saturated calomel reference electrode (SCE) and an inert-gas inlet. Dry degassed dichloromethane containing 0.1 mol dm^{-3} NBu_4PF_6 as the background electrolyte was used as the solvent. The scan rate applied was 100 mV^{-1} s^{-1}. The measurements were controlled by a microcomputer using a Condecon 310 cyclic voltammetry program. The apparatus was an EG & G Princeton Applied Research Model 264A polarographic analyser (stripping voltammeter connected to an EG & G Condecon 300 controller). The current *vs.* voltage curves were recorded with a Philips X-Y recorder. The apparatus was always calibrated using compounds of known redox properties (*e.g.* ferrocene or ttf).

Syntheses.—*4,5-Bis(ferrocenylmethylsulfanyl)-1,3-dithiole-2-thione* **4**. Oxalyl chloride (0.88 cm^3, 1.27 g, 10 mmol) was added to a solution of 1-ferrocenylmethanol (2.16 g, 10 mmol) in dry dichloromethane (200 cm^3) and the mixture stirred under nitrogen at room temperature for 1.5 h. After removing the solvent and unreacted oxalyl chloride under high vacuum, the product was redissolved in dry dichloromethane and added to a solution of $[NEt_4]_2[Zn(C_3S_5)_2]$ (1.37 g, 2.5 mmol) in dry dichloromethane (100 cm^3). The mixture was refluxed under nitrogen for 10 h. After allowing to cool to room temperature, the mixture was filtered through a silica gel plug, washed extensively with dichloromethane and the solvent removed on a rotary evaporator to reveal a viscous red oil. Purification of the crude product was best effected by column chromatography on a silica gel support using light petroleum–dichloromethane (70:30) as the eluent. After removing the solvents on a rotary evaporator a fibrous red solid was obtained. Yield = 0.84 g (14%), m.p. 103–105 °C (Found: C, 50.60; H, 3.85. Calc for $C_{25}H_{22}Fe_2S_5$: C, 50.55; H, 3.70%). NMR (250 MHz): ^{1}H, δ 3.70 (s, 2 H), 4.18 (s, 5 H) and 4.19 (s, 4 H). ^{13}C, δ 37.55 (CH$_2$), 68.47, 68.72, 82.53 (ferrocenyl), 137.75 (C=C), and 211.74 (C=S). IR (CH_2Cl_2): 1064.2 cm^{-1} (C=S). FAB mass spectrum: *m/z* 594 (M^+). UV/VIS (CH_2Cl_2): λ_{max}(ln ε) 234 (10.17) and 378 nm (9.47).

4,5-Bis(ferrocenylmethylsulfanyl)-1,3-dithiol-2-one **5**. The same procedure was employed as for the preparation of compound **4** but using $Cs_2[C_3OS_4]$ instead of $[NEt_4]_2[Zn(C_3S_5)_2]$. As for **4**, purification was best effected by column chromatography on a silica gel support using light petroleum–dichloromethane (70:30) as the eluent. After removing the solvents on a rotary evaporator a red-brown powder was obtained. Yield = 1.51 g (20%), m.p. 95–98 °C (Found: C, 50.45; H, 3.80. Calc for $C_{25}H_{22}Fe_2OS_4$: C, 51.90; H, 3.80%). NMR (250 MHz): ^{1}H, δ 3.70 (s, 2 H), 4.18 (s, 5 H) and 4.19 (s, 4 H); ^{13}C, δ 37.36 (CH$_2$), 68.39, 68.74, 82.84 (ferrocenyl), 128.76 (C=C) and 189.93 (C=O). IR (CH_2Cl_2): 1667.7 cm^{-1} (C=O). FAB mass spectrum: *m/z* 578 (M^+). UV/VIS (CH_2Cl_2): λ_{max}(ln ε) 231 (10.17) and 373 nm (9.39).

Tetra(ferrocenylmethylsulfanyl)tetrathiafulvalene **6**. Compound **4** (0.50 g) was suspended in freshly distilled triethyl phosphite (15 cm^3) under nitrogen. The stirred reaction mixture was heated at between 110 and 120 °C for 45 min, then cooled to room temperature whereupon methanol was added to precipitate a red solid. After decanting off the triethyl phosphite, the red solid was redissolved in chloroform and the excess of phosphite removed under high vacuum. The product was filtered through a silica gel plug using dichloromethane, the solvent was concentrated and the product recrystallised from dichloromethane–hexane at −20 °C. After filtering the solution, an orange powder was obtained. Yield = 0.15 g (16%), m.p. 75–77 °C (Found: C, 53.20; H, 4.30. Calc. for $C_{50}H_{44}Fe_4S_8$: C, 53.40; H, 3.90%). NMR (400 MHz): ^{1}H, δ 3.73 (s, 2 H), 4.14 (t, 2 H), 4.15 (s, 5 H) and 4.19 (t, 2 H); ^{13}C, δ 36.83 (CH$_2$), 68.21, 68.70, 68.74, 83.39 (ferrocenyl), 110.20 (C=C) and 129.15 (C=C). IR ($CHCl_3$): 822, 1000, 1105 and 1413 cm^{-1}. FAB mass spectrum: *m/z* 1124 (M^+ − H). UV/VIS (CH_2Cl_2): λ_{max}(ln ε) 230 (11.28), 332 (7.44) and 404 nm (6.48).

Tetraphenylphosphonium bis[1,2-bis(ferrocenylmethylsulfanyl)ethene-1,2-dithiolato] nickelate **8**. To a slurry of compound **5** (0.30 g, 0.52 mmol) in ethanol was added dropwise sodium metal (0.024 g, 1.04 mmol) in ethanol under an inert atmosphere. The mixture was stirred at room temperature sealed under nitrogen for 15 h until a deep brown colouration was obtained. The solution was quickly filtered into an ethanolic solution of the counter cation, tetraphenylphosphonium bromide (0.22 g, 0.52 mmol) and then $NiCl_2{\cdot}6H_2O$ (0.062 g, 0.26 mmol) in ethanol was added dropwise. The resulting green solid was filtered off, washed with ethanol and dried *in vacuo*. Yield = 0.32 g (46%) (Found: C, 55.20; H, 5.50. Calc. for $C_{72}H_{64}Fe_4NiPS_8$: C, 56.05; H, 5.25%). FAB mass spectrum: *m/z* 988 (M^+), 775, 650, 483 and 461. NIR (CH_2Cl_2): λ_{max} 1250 nm.

Crystal Structure Determination of Compound **6**.—*Crystal data.* $C_{50}H_{44}Fe_4S_8{\cdot}0.5C_8H_{18}$, $M = 1181.84$, monoclinic, space group $P2_1/a$, $a = 9.483(3)$, $b = 27.8536(9)$, $c = 10.5534(9)$ Å, $\beta = 105.42(2)°$ (by least-squares refinement of the setting angles for 250 reflections having $\theta = 2.34$–$25.09°$), $U = 2687.2(9)$ Å^3, $Z = 2$, $D_c = 1.461$ g cm^{-3}, $T = 298$ K, μ(Mo-Kα) = 14.04 cm^{-1}, $F(000) = 1218$, crystal size = 0.10 × 0.03 × 0.02 mm.

Data were collected on a FAST TV Area detector diffractometer following previously described methods.[26] From the ranges scanned, 10 572 data were recorded ($2.34 \leqslant \theta \leqslant 25.09°$; $-8 \leqslant h \leqslant 10$, $-31 \leqslant k \leqslant 31$, $-11 \leqslant l \leqslant 12$) and merged to give 4074 unique ($R_{int} = 0.075$).

The structure was solved *via* direct methods [27] and refined by F_o^2 by full-matrix least squares[28] using all unique data corrected for Lorentz and polarisation factors and also for absorption[29] (minimum and maximum absorption correction factors 0.887 and 1.097). All non-hydrogen atoms were anisotropic. Within the unit cell, each molecule of compound **6** was accompanied by a half-occupied solvent molecule of what appeared to be a centrosymmetric octane chain. The four unique carbon atoms of this molecule were also treated anisotropically but it was necessary to restrain their displacement coefficients by using the instruction ISOR 0.01 0.02 in the refinement procedure.[28] The hydrogens of the solvent were ignored and those on the complex molecule were included in idealised positions with U_{iso} free to refine. The weighting scheme was $w = 1/[\sigma^2(F_o)^2 + (0.0777P)^2]$, where $P = [\max(F_o)^2 + 2(F_c)^2]/3$; this gave satisfactory agreement analyses. Final R_1 (on F) and wR_2 (on F_o^2) values were 0.1053 and 0.1343 for all 4074 data and 338 parameters. The corresponding R values were 0.0537 and 0.1248 for 2001 data with $I > 2\sigma(I)$. Sources of scattering factors were as in ref. 28. The fractional atomic coordinates are listed in Table 1, selected bond lengths and angles in Table 2. The numbering of the atoms is shown in Fig. 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Syntheses.—The synthesis of compound **4** and its ketone analogue **5** is shown in Scheme 1. Lithium aluminium hydride reduction of ferrocenecarbaldehyde **1** in diethyl ether gave 1-ferrocenylmethanol **2**. (Chloromethyl)ferrocene **3** was prepared by the reaction of oxalyl chloride with **2** in dry dichloromethane. After removal of unreacted oxalyl chloride *in vacuo*, compounds **4** and **5** were prepared by refluxing **3** with $[NEt_4]_2[Zn(C_3S_5)_2]$ and $Cs_2[C_3OS_4]$ respectively in dry dichloromethane overnight.

Conventional coupling of compound **4** in neat triethyl

Table 1 Atomic coordinates (× 10^4) for compound **6**

Atom	*x*	*y*	*z*
Fe(1)	2 436.0(9)	1 670.1(3)	4 313.7(10)
Fe(2)	8 731.2(9)	635.7(3)	7 922.0(8)
S(1)	6 350(2)	1 517(1)	2 359(2)
S(2)	8 028(2)	592(1)	4 203(2)
S(3)	5 086(2)	779(1)	298(2)
S(4)	6 723(2)	−17(1)	1 858(2)
C(1)	3 905(8)	1 289(3)	5 690(9)
C(2)	4 611(7)	1 572(2)	4 959(8)
C(3)	4 109(6)	1 432(2)	3 629(7)
C(4)	3 113(7)	1 065(2)	3 562(9)
C(5)	2 988(8)	980(3)	4 861(9)
C(6)	1 205(14)	2 089(4)	5 236(16)
C(7)	2 037(13)	2 362(4)	4 655(20)
C(8)	1 682(15)	2 264(5)	3 336(19)
C(9)	599(13)	1 913(5)	3 062(15)
C(10)	331(10)	1 813(4)	4 286(18)
C(11)	4 507(6)	1 653(2)	2 496(7)
C(12)	6 174(6)	921(2)	1 874(5)
C(13)	6 897(5)	551(2)	2 600(6)
C(14)	6 747(6)	362(2)	5 064(5)
C(15)	5 364(5)	154(2)	444(5)
C(16)	7 506(5)	222(2)	6 426(6)
C(17)	6 902(6)	220(2)	7 520(6)
C(18)	7 929(6)	37(3)	8 618(7)
C(19)	9 202(7)	− 72(2)	8 230(6)
C(20)	8 951(6)	40(2)	6 895(6)
C(21)	10 169(11)	1 146(3)	7 678(12)
C(22)	10 431(11)	1 031(3)	9 006(12)
C(23)	9 167(14)	1 131(3)	9 403(10)
C(24)	8 090(12)	1 302(3)	8 310(13)
C(25)	8 723(11)	1 315(3)	7 242(10)
C(01)*	4 859(41)	2 285(11)	−1 538(31)
C(02)*	3 663(47)	2 238(11)	−938(27)
C(03)*	2 389(34)	2 402(9)	−561(23)
C(04)*	1 051(53)	2 513(13)	−829(35)

* Atom in the half-occupied octane solvent molecule.

Table 2 Selected bond lengths (Å) and angles (°)

Fe(1)–C(8)	1.981(9)	Fe(1)–C(9)	2.004(9)
Fe(1)–C(2)	2.011(6)	Fe(1)–C(10)	2.028(8)
Fe(1)–C(1)	2.025(7)	Fe(1)–C(3)	2.022(5)
Fe(1)–C(7)	2.015(10)	Fe(1)–C(4)	2.038(7)
Fe(1)–C(5)	2.036(7)	Fe(1)–C(6)	2.068(10)
Fe(2)–C(20)	2.023(6)	Fe(2)–C(25)	2.023(8)
Fe(2)–C(21)	2.032(8)	Fe(2)–C(17)	2.034(6)
Fe(2)–C(19)	2.029(7)	Fe(2)–C(24)	2.028(8)
Fe(2)–C(22)	2.034(8)	Fe(2)–C(23)	2.043(8)
Fe(2)–C(16)	2.048(6)	Fe(2)–C(18)	2.048(7)
S(1)–C(12)	1.732(6)	S(1)–C(11)	1.831(6)
S(2)–C(13)	1.749(6)	S(2)–C(14)	1.816(5)
S(3)–C(12)	1.753(6)	S(3)–C(15)	1.760(6)
S(4)–C(13)	1.753(6)	S(4)–C(15)	1.759(5)
C(3)–C(11)	1.480(8)	C(12)–C(13)	1.357(8)
C(14)–C(16)	1.478(7)	C(15)–C(15^{I})	1.323(10)
C(12)–S(1)–C(11)	101.7(3)	C(13)–S(2)–C(14)	98.1(3)
C(12)–S(3)–C(15)	95.9(3)	C(13)–S(4)–C(15)	95.5(3)
C(4)–C(3)–C(11)	125.7(7)	C(2)–C(3)–C(11)	126.7(6)
C(3)–C(11)–S(1)	115.6(4)	C(13)–C(12)–S(1)	124.5(4)
C(13)–C(12)–S(3)	116.5(4)	S(1)–C(12)–S(3)	118.9(4)
C(12)–C(13)–S(2)	125.8(5)	C(12)–C(13)–S(4)	117.4(4)
S(2)–C(13)–S(4)	116.9(4)	C(16)–C(14)–S(2)	111.2(4)
C(15^{I})–C(15)–S(4)	123.4(6)	C(15^{I})–C(15)–S(3)	122.9(6)
S(4)–C(15)–S(3)	113.6(3)	C(17)–C(16)–C(14)	126.4(5)
C(20)–C(16)–C(14)	127.5(5)		

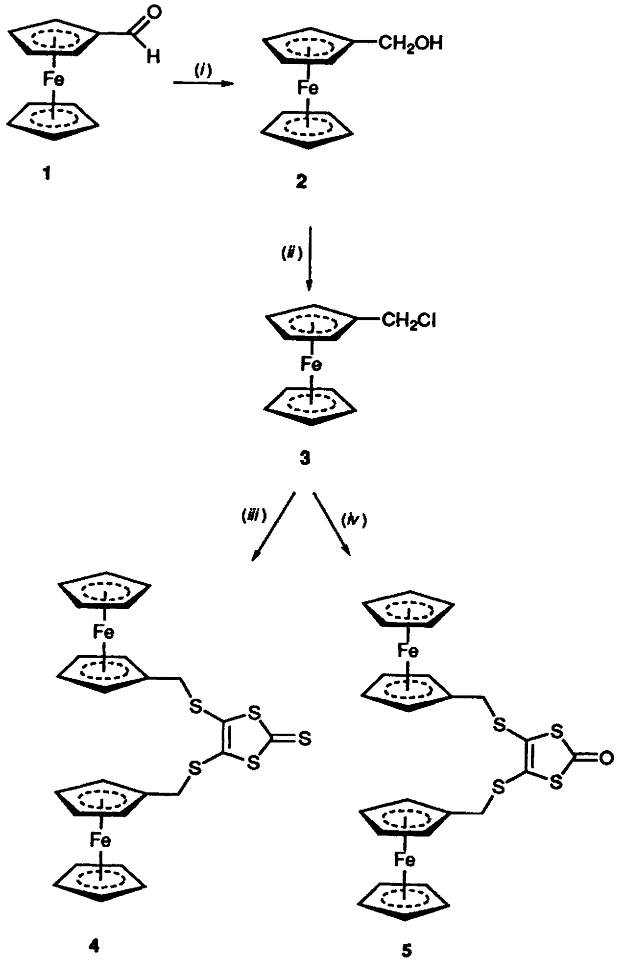
Geometry of the C_5H_5 rings C–C 1.353(12)–1.427(9), average 1.396 C–C–C 104.6(12)–109.9(12), average 108.0. Symmetry transformation used to generate equivalent atoms: I $-x + 1, -y, -z$.

phosphite yielded the tetra(ferrocenylmethylsulfanyl)tetrathiafulvalene donor **6** as shown in Scheme 2.

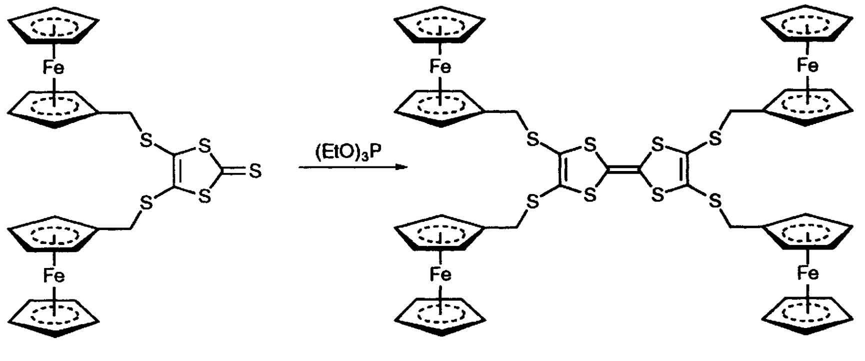
The metal complex formation reaction of compound **5** is depicted in Scheme 3. Treatment of the ketone **5** with sodium ethoxide under nitrogen required more than 15 h of vigorous stirring at room temperature in order to open the ketone ring and generate the disodium salt **7**. This intermediate afforded the corresponding complex **8** on treatment with tetraphenylphosphonium bromide, followed by addition of exactly half an equivalent of $NiCl_2 \cdot 6H_2O$. Metal complexes of dithiolene ligands are known to form anionic and neutral complexes with formal charges of −2, − 1 and 0.[30] In the present study only the monoanionic complex **8** was isolated. With Ni^{2+} the dianionic complex would be expected to form initially, at least, but although the reactions were carried out under an inert atmosphere up to the complex-formation stage, the dianionic species oxidised spontaneously during work-up. This is not surprising in view of the fact that dithiolene complexes are susceptible to oxidation by oxygen.

The FAB mass spectrum of complex **8** is shown in Fig. 1. Dithiolene complexes are known to have low volatility, decomposing near the melting point[18] and therefore the fragmentation patterns are generally very complex for anything other than simple dithiolenes. Although the molecular ion peak for complex **8** of *m*/*z* 1158 does not appear in the FAB mass spectrum, the correct fragmentation pattern clearly appears, showing molecular ion peaks for three (*m*/*z* 988) and two (*m*/*z* 775) ferrocenyl ligands which are connected to the metal dithiolene core.

The structures of all these new air-stable compounds were characterised by elemental analysis, NMR and IR spectroscopy and FAB mass spectrometry (see Experimental section).

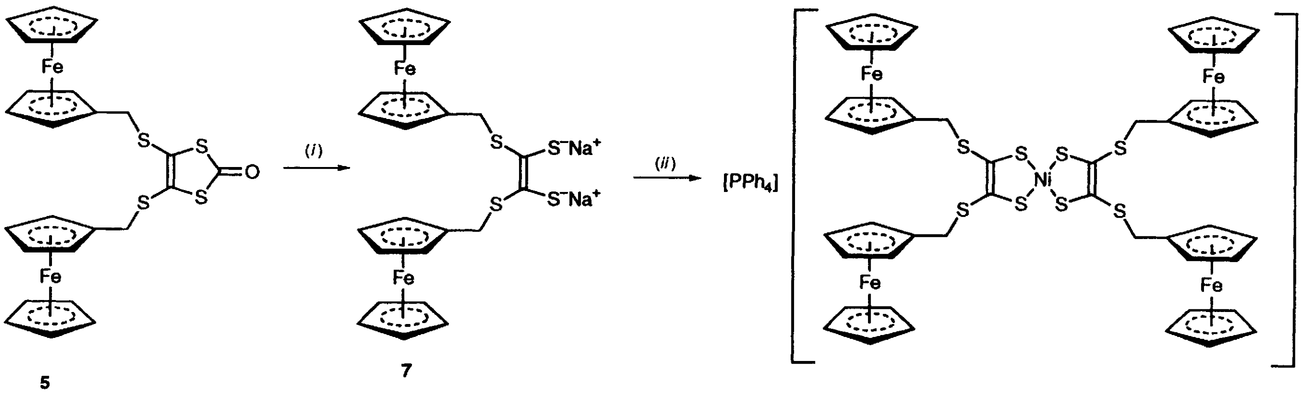


Scheme 1 (*i*) $LiAlH_4$; (*ii*) oxalyl chloride; (*iii*) $[NEt_4]_2[Zn(C_3S_5)_2]$; (*iv*) $Cs_2[C_3OS_4]$



4 **6**

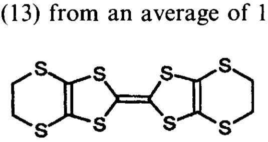
Scheme 2



5 **7** **8**

Scheme 3 (*i*) NaOEt; (*ii*) (*a*) [PPh$_4$]Br, (*b*) NiCl$_2$·6H$_2$O

Crystal Structure of Compound **6**.—Orange single crystals of compound **6** suitable for X-ray diffraction investigations were obtained by the technique of dichloromethane–hexane (1:2) layering at room temperature. The structure which is centrosymmetric is shown in Fig. 2. This also illustrates the relative orientations of the ferrocene units with respect to the central ttf moiety. The relevant bond lengths and angles are summarised in Table 2. On comparing the structure to that of the extended ttf analogue bis(ethylenedithio)tetrathiafulvalene (bettf)[31] the presence of the peripheral ferrocene units lengthens C(12)–C(13) from an average of 1.331 Å in bettf to 1.357 Å in **6**. The central C=C bond in **6** is shorter by 0.012 Å than that observed in bettf. In each of the ferrocene units the two cyclopentadienyl rings are eclipsed and coplanar. The central ttf unit is planar within 0.063 Å and each ferrocene ligand is twisted out of the plane of the ttf core due to the presence of the CH$_2$ linking units. The random orientation of the ferrocene units means that there are no intermolecular S···S contacts less than twice the van der Waals radius for sulfur of 3.70 Å. Although good intermolecular orbital overlap of the sulfur atoms in the solid state is a usual prerequisite for electrical conduction, the lack of short S···S contacts does not necessarily preclude the possibility that charge-transfer salts of **6** will show high room-temperature conductivities.[32]



bettf

NIR Studies on Complex **8**.—Metal dithiolenes display an intense electronic transition in the near-IR region, the origin of which was discussed by Mueller-Westerhoff and co-workers.[17,18] He considered the square-planar nickel group dithiolenes to possess low-lying empty π molecular orbitals comprising various metal and ligand characters. The intense NIR absorption arises from a transition between the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) states.

The 'ground-state' metal dithiolene is considered to be the neutral [Ni(edt)$_2$] complex with a HOMO – LUMO energy gap ΔE as shown in Fig. 3(*a*). Shifting the HOMO – LUMO relative energies such that ΔE decreases is the key to obtaining complexes with absorption at lower energy. The presence of electron-withdrawing R groups on the metal bis(dithiolene) unit leads to stabilisation of the HOMO and LUMO by approximately equal amounts ($\Delta E \approx \Delta E_A$) [Fig. 3(*b*)] which does not appreciably shift the electronic transition. Electron-donating R groups destabilise the HOMO more than the LUMO ($\Delta E > \Delta E_D$) [Fig. 3(*c*)], resulting in a bathochromic shift of the absorption maximum.

There are several important factors which need to be considered in any attempt to shift the absorption maximum of dithiolenes to lower energy:[17] (1) the presence of an extended π system in the molecule; (2) the presence of electron-donating substituents on the molecule; (3) coplanarity of the ligand π system and the metal dithiolene core. By altering the nature of the R groups and the central metal it is possible to synthesise complexes which absorb at specific wavelengths, *i.e.* 'fine-tuning' the absorption maximum. This has many applications, especially in the area of non-linear optics and telecommunications.

Compared with the absorption of certain nickel dithiolene compounds,[18,30] for example [Ni(edt)$_2$] absorbs at 720 nm in hexane,[33] the absorption maximum for complex **8**, in dichloromethane, is at a considerably lower energy and occurs

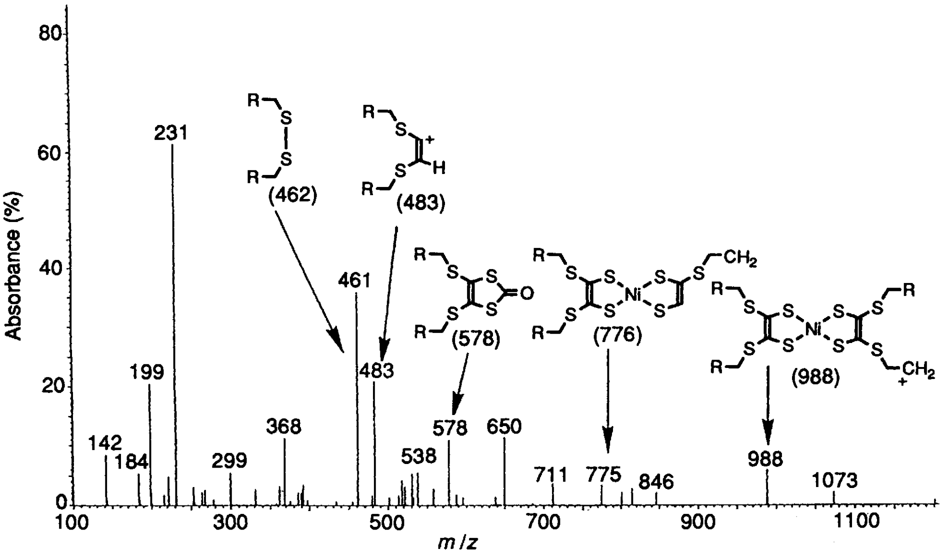
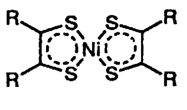


Fig. 1 Fast atom bombardment mass spectrum of complex **8**; R = ferrocenyl



[Ni(edt)$_2$] when R = H

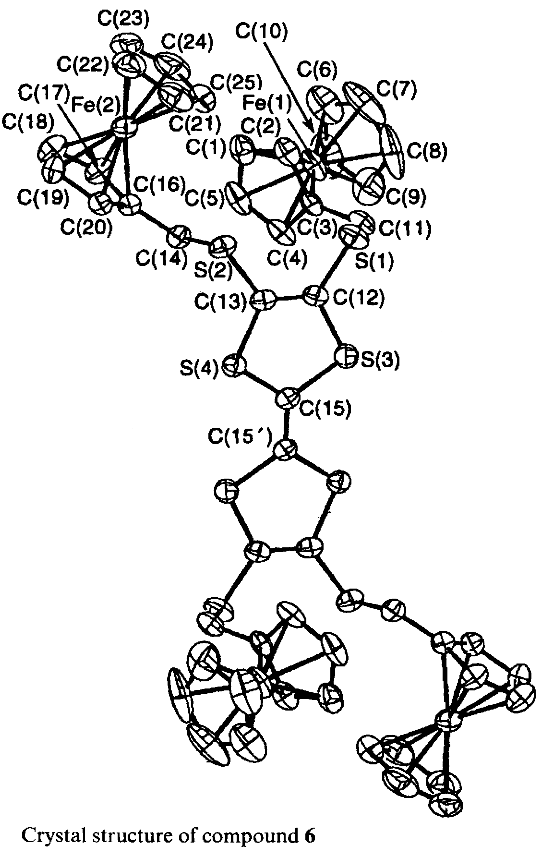


Fig. 2 Crystal structure of compound **6**

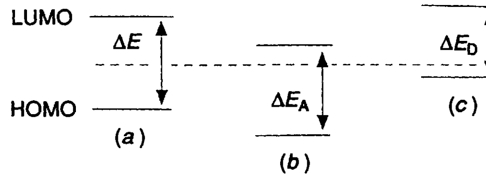


Fig. 3 Frontier orbitals in metallic dithiolene complexes

at 1250 nm (ln ε = 9.62) (Fig. 4). This absorption band in monoanionic dithiolenes is associated with a transition from the highest-energy filled π orbital of the molecular complex, NHOMO ($2b_{1u}$), to the highest-energy half-filled molecular orbital, HOMO ($3b_{2g}$).[33,34] It is of lower energy than might be expected because there exists no possibility for the ferrocenes to adopt a coplanar configuration with the dithiolene core, suggesting very little interaction between the two moieties. It would, however, seem that the electron-donating properties of the ferrocene substituents are able to transmit effectively through the non-conjugated CH_2 spacer-links resulting in this large shift in the NIR region as compared with simple dithiolene systems. We are presently working on incorporating a conjugated link between the ferrocenes and dithiolene core, thus possibly shifting the NIR absorption maximum towards the 1500 nm region, thereby enhancing its potentially useful optical properties.

Electrochemical Studies.—The electrochemistry of compounds **4** and **5** and of the corresponding organic donor **6** were investigated using cyclic voltammetry. The results together with the corresponding half-wave potentials for ferrocene, ttf and bettf (recorded under the same conditions) are given in Table 3.

The ferrocene groups in compounds **4** and **5** have a half-wave potential of +564 and +560 mV respectively compared with +471 mV for ferrocene. This shift in potential compared to ferrocene is due to the electron-withdrawing effect of the neighbouring multisulfur ring system in **4** and **5** with π electrons of the cyclopentadienyl rings able to delocalise into vacant d orbitals of the sulfur atoms.

In the related organic donor **6** the electron-donating effect of the central ttf moiety upon each ferrocene ligand is negligible. This is evident from ^1H NMR studies which show that the ferrocenyl signals for compounds **4** and **6** are of similar field strength (see Experimental section). Therefore, in the CV of **6** (Fig. 5) the first oxidation peak can be attributed to the process $[Fe(\eta^5-C_5H_5)_2] \longrightarrow [Fe(\eta^5-C_5H_5)_2]^+$ by comparison to the half-wave potential for **4**. Oxidation of the four ferrocene groups appears to occur at the same potential, suggesting that the CH_2 spacer units prevent electronic interactions between the ferrocene groups. Based upon the difference between the $E_{\frac{1}{2}}$ value for the process $ttf^+ \rightleftharpoons ttf^{2+}$ in bettf (+929 mV) and **6** (+1059 mV), the redox process $ttf \rightleftharpoons ttf^+$ in **6** is expected to

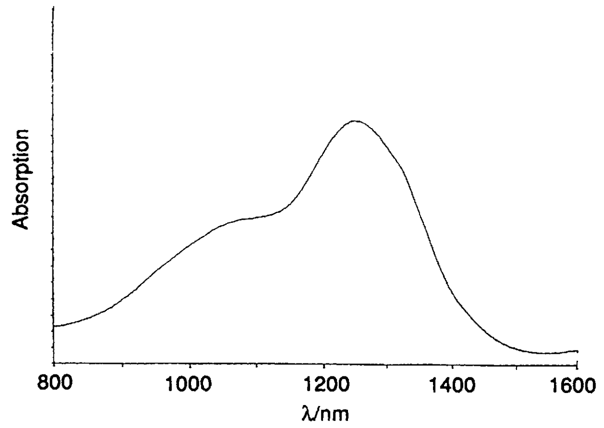


Fig. 4 The NIR spectrum of complex **8**

occur at a similar potential to that of the oxidation of ferrocene groups. This explains the broadening of the ferrocene ⟶ ferrocenium oxidation peak between 600 and 650 mV. Both the first and second oxidations of the ttf moiety in **6** occur at a higher potential than for ttf and bettf. This is because the oxidation of ferrocene to ferrocenium in **6** increases the positive charge on the ferrocene ligands which in turn reduces electron density within the central ttf moiety, thus making it more difficult to oxidise. This high oxidation potential of the central ttf moiety in **6** indicates that charge-transfer complexation with acceptors such as tetracyanoquinodimethane (tcnq) and partially oxidised salts with inorganic anions may not occur.

Conclusion

New types of molecular materials containing ttf and metal dithiolene units attached to ferrocene ligands have been prepared and their properties investigated. The chemistry of ferrocenes and sulfur-based ligands combined together within one molecular unit offers a new perspective in the design and development of materials exhibiting novel electrical conduction, optical and magnetic properties. The design of such materials should lead to: (1) the development of third-order NLO materials with enhanced responses, due to extensive delocalisation, in the 1.3 and 1.5 μm regions; (2) compounds containing several magnetic centres with varying degrees of interaction depending on the nature of the linkage between the ferrocene and dithiolene units; this will result in unusual magnetic and electronic properties; (3) applications in molecular sensors; (4) the development of new layered structures containing interacting magnetic centres capable of forming inclusion compounds with a variety of molecules.

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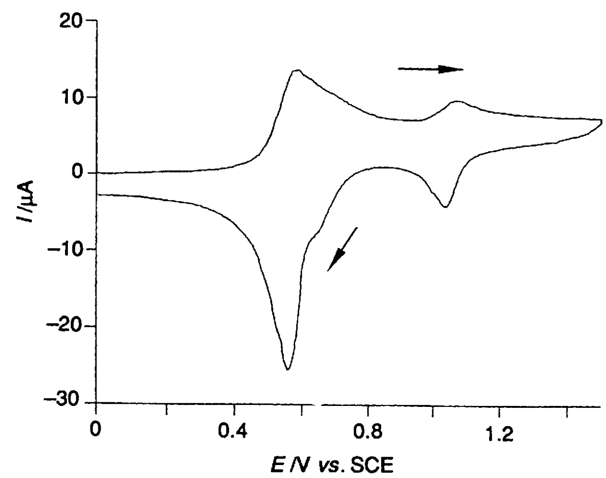

Fig. 5 Cyclic voltammogram of compound **6**

Table 3 Half-wave redox potentials ($E_{\frac{1}{2}}$/mV) for ferrocene, ttf, bettf and compounds **4**–**6**

	Redox process		
Compound	$Fe^{II} \longrightarrow Fe^{III}$	$ttf \longrightarrow ttf^+$	$ttf^+ \longrightarrow ttf^{2+}$
Ferrocene	+471		
ttf		+410	+777
bettf		+516	+929
4	+564		
5	+560		
6	+572	*	+1059

* Oxidation peak obscured.

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