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Electron-transfer salts derived from *N*,*N*′-dicyano-*p*-benzoquinone diimines and the novel dinuclear organometallic donor [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] †

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Reaction of the electron-rich sulfido-bridged complex [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] with electron-acceptor *N*,*N*′-dicyano-*p*-benzoquinone diimines resulted in electron transfer and formation of crystalline 1 : 1 salts of general formula [donor cation][acceptor anion]. The crystal structures of [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] and [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$][dmdcnqi] (dmdcnqi = *N*,*N*′-dicyano-2,5-dimethyl-*p*-benzoquinone diimine) have been determined by X-ray diffraction methods. The neutral donor molecule possesses exact C_2 symmetry, the molecules stacking in linear chains in the crystal with the C_5Me_5 rings of adjacent molecules parallel to each other. The donor cations in the electron-transfer salt also possess exact C_2 symmetry and, moreover, are arranged similarly in the crystal, but with the planar acceptor anions sandwiched between the C_5Me_5 rings and at an angle of 11.4° to these rings. The sequence along the rows is thus one of alternating donor cations ($D^{\bullet +}$) and acceptor anions ($A^{\bullet -}$), *i.e.* $\cdots D^{\bullet +}A^{\bullet -}D^{\bullet +}A^{\bullet -}D^{\bullet +}A^{\bullet -}\cdots$. Consistent with the formation of radical cations and anions is a decrease in the Fe $\cdots$ Fe distance from 3.445(1) Å in the neutral donor molecule to 3.083(2) Å in the donor cation. However, the temperature dependence of the magnetic susceptibility of this salt, when fitted by the Curie–Weiss law, affords a Weiss constant (θ) of only 0.414 K, which suggests that there is little ferromagnetic coupling between the unpaired spins on the radical cations and anions.

There is considerable interest in the synthesis and characterisation of molecular/organic polymer-based materials that exhibit co-operative magnetic interactions such as ferromagnetism,[1] an example of a material that behaves as a room-temperature molecular magnet being amorphous [V(tcne)$_x$]·$y$$CH_2Cl_2$ ($x \approx 2, y \approx 0.5$, tcne = tetracyanoethylene).[2] The best-studied crystalline group of compounds in this category are electron-transfer salts derived from electron-rich metallocene donors and electron-acceptor molecules such as tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane (tcnq) with [Fe(η-C_5Me_5)$_2$]$^{\bullet +}$[tcne]$^{\bullet -}$ a bulk ferromagnet with a Curie temperature, T_c, of 4.8 K,[3] being a well characterised example. The related manganese compound [Mn(η-C_5Me_5)$_2$]$^{2\bullet +}$-[tcnq]$^{\bullet -}$ also behaves as a bulk ferromagnet with a T_c of 6.2 K.[4] A structural feature common to this group of compounds is that they possess parallel $\cdots D^{\bullet +}A^{\bullet -}D^{\bullet +}A^{\bullet -}D^{\bullet +}A^{\bullet -}\cdots$ linear chains of donor cations ($D^{\bullet +}$) and acceptor anions ($A^{\bullet -}$), an unpaired electron being present on each ion.

We were interested in establishing the effect of changing the metallocene donor on the crystal structures and physical properties of their electron-transfer salts with planar polycyano hydrocarbon acceptors. Miller and co-workers[1] had systematically probed the structure–function relationship by modifying the metallocene donor through substitution of the methyl groups on the C_5 ring with hydrogen, and through use of a selection of third-, fourth- and fifth-row transition-metal ions. However, in all these cases, the metallocene donor is *mono*nuclear; our intention was to investigate the reactions of a *di*nuclear metallocene donor with typical acceptors. Thus we have shown that the diphosphazane ligand-bridged dimer [Fe_2(cp)$_2$(μ-CO)$_2${μ-Ph_2PN(Et)PPh_2}] (cp = η-C_5H_5) reacts with tcnq to afford [Fe_2(cp)$_2$(μ-CO)$_2${μ-Ph_2PN(Et)PPh_2}]$_2$-[tcnq]$_3$·2MeCN, as confirmed X-ray crystallographically.[5] More recently, the dinuclear donor that we have employed is the sulfido-bridged derivative *cis*-[Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] **1** in which two ‘half-sandwich’ Fe(C_5Me_5)$_2$(CO) units are linked by two bridging ethylsulfanyl groups. This complex is sufficiently electron-rich to ensure complete electron transfer in its reactions with typical electron-acceptor molecules. Structurally, it is distinguished from a mononuclear metallocene analogue, such as decamethylferrocene, by the presence of two cyclopentadienyl rings which are not parallel to each other and which are separated by a larger distance than in the mononuclear species. It was therefore of interest to investigate the packing of the cations and anions in crystals of an electron-transfer salt of [**1**]$^{\bullet +}$ with a planar acceptor anion and, indeed, whether integrated stacks of cations and anions would form in the first place. We have treated **1** with various *N*,*N*′-dicyano-*p*-benzoquinone diimines, as well as with tcne and tcnq. The results of the former reactions are given here; those with tcne and tcnq will be reported in a subsequent paper. Also reported here are the crystal structures of [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$][dmdcnqi] **2** (dmdcnqi = *N*,*N*′-dicyano-2,5-dimethyl-*p*-benzoquinone diimine) and of **1** itself for comparison.

Experimental

Commercially available starting materials, [Fe_2(η-C_5Me_5)$_2$(μ-CO)$_2$(CO)$_2$] (Strem) and diethyl disulfide (Aldrich), were used without further purification. *N*,*N*′-Dicyano-, *N*,*N*′-dicyano-2-methyl-, *N*,*N*′-dicyano-2,5-dimethyl- and 2-chloro-*N*,*N*′-dicyano-5-methyl-*p*-benzoquinone diimine (dcnqi, mdcnqi, dmdcnqi and cmdcnqi) were synthesised according to published procedures.[6] Solvents were dried using standard reagents[7] and distilled prior to use.

Infrared data were recorded on a Shimadzu FTIR-4300 spectrophotometer in dichloromethane and as KBr discs, ^1H NMR spectra on a Varian Gemini 200 spectrophotometer (chemical shifts are quoted relative to $SiMe_4$). The C, H and N analyses were performed by Galbraith Laboratories, Knoxville, TN, USA. Electrochemical studies were carried out using a PAR model 173 potentiostat in conjunction with a three-

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

electrode cell. The auxilliary electrode was a platinum wire and the working electrode a platinum disc. The reference electrode was a silver wire coated with silver chloride and immersed in a CH_2Cl_2 solution containing 0.1 mol dm^{-3} $[NBu_4][ClO_4]$ and separated from the test solution by a fine-porosity frit. The CH_2Cl_2 solutions were 1×10^{-3} mol dm^{-3} in compound and 0.1 mol dm^{-3} in $[NBu_4][ClO_4]$ as the supporting electrolyte. Under these conditions the E° value for the $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ couple used as an internal standard was 0.44 V.

Syntheses

$[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$ 1. Diethyl disulfide (0.18 cm^3, 1.49 mmol) was added to a suspension of $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)_2(CO)_2]$ (0.47 g, 0.96 mmol) in toluene (50 cm^3) and the mixture heated under reflux for 22 h. Following cooling of the solution the solvent was removed *in vacuo*, the residue extracted with light petroleum (b.p. 60–80 °C) and the volume of the extract subsequently reduced by application of a vacuum. Storage of this solution at 0 °C overnight resulted in the separation of brown-black crystals of the product. Yield: *ca.* 0.40 g, 75% (Found: C, 55.7; H, 7.15. $C_{26}H_{40}Fe_2O_2S_2$ requires C, 55.7; H, 7.20%). ^1H NMR (room temperature): δ 1.79 (s, 30 H, C_5Me_5), 2.32 (q, 4 H, SCH_2CH_3) and 1.16 (t, 6 H, SCH_2CH_3).

$[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$[dmdcnqi] 2. A solution of compound **1** (0.100 g, 0.18 mmol) in toluene (70 cm^3) was added dropwise to a stirred solution of dmdcnqi (0.033 g, 0.18 mmol) in toluene (50 cm^3) at 0 °C. The solution changed from yellow-brown to green during the addition. The green solution was allowed to warm to room temperature and its volume reduced *in vacuo*; this resulted in the precipitation of crude product as a blue-black solid. This material was filtered off, washed with diethyl ether and dried *in vacuo*. Extraction of the material with acetonitrile, followed by reduction of the volume of the combined extracts *in vacuo*, cooling of the solution to *ca.* −15 °C and storage of the solution at this temperature for 3 d, resulted in the separation of the pure product as shiny blue-black crystals. Yield: *ca.* 0.08 g, 66% (Found: C, 58.75; H, 6.55; N, 7.70. $C_{36}H_{48}Fe_2N_4O_2S_2$ requires C, 58.05; H, 6.50; N, 7.55%).

$[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$[cmdcnqi] 3. A solution of compound **1** (0.042 g, 0.075 mmol) in methylcyclohexane (12 cm^3) was added dropwise to a stirred solution of cmdcnqi (0.015 g, 0.071 mmol) in dichloromethane (8 cm^3) at room temperature. On completion of the addition the volume of the reaction mixture was reduced to *ca.* 3 cm^3 *in vacuo* and stored overnight at *ca.* 0 °C; this resulted in the precipitation of a decomposition product as well as a small amount of the desired product. The precipitate was filtered off and the volume of the filtrate reduced *in vacuo*. Storage of this solution at 0 °C overnight led to the separation of shiny blue-black crystals of analytically pure product. Yield: *ca.* 0.017 g, 30% (Found: C, 54.4; H, 5.20; N, 7.35. $C_{35}H_{45}ClFe_2N_4O_2S_2$ requires C, 54.95; H, 5.95; N, 7.30%).

$[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$[mdcnqi] 4. A solution of compound **1** (0.050 g, 0.089 mmol) in methylcyclohexane (15 cm^3) was added dropwise to a stirred solution of mdcnqi (0.041 g, 0.082 mmol) in toluene (6 cm^3) at room temperature. Following the addition a blue-black precipitate formed which was filtered off, washed with light petroleum and dried *in vacuo*. The material thus obtained was microcrystalline and analytically pure. Yield: *ca.* 0.042 g, 65% (Found: C, 58.0; H, 6.25; N, 8.25. $C_{35}H_{45}Fe_2N_4O_2S_2$ requires C, 57.55; H, 6.20; 7.70%).

$[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$[dcnqi] 5. A solution of compound **1** (0.040 g, 0.071 mmol) in toluene (15 cm^3) was added dropwise to a stirred solution of dcnqi (0.011 g, 0.071 mmol) in toluene (10 cm^3) at room temperature. Following the addition the reaction mixture was stirred for 1 h. At this stage a small amount of product had precipitated; this was redissolved by the addition of a small amount of acetonitrile. The volume of the solution was reduced *in vacuo* and the solution stored at *ca.* − 15 °C for 36 h. This resulted in the precipitation of the desired product as aggregates of very small dark blue plate-like crystals together with small quantities of a brown powdery decomposition product. The crystals of the desired product were separated manually from the brown material. Yield: *ca.* 0.025 g, 50% (Found: C, 57.1; H, 5.95; N, 7.50. $C_{34}H_{42}Fe_2N_4O_2S_2$ requires C, 57.0; H, 6.20; N, 7.80%).

Crystallography

Diffractometer data for $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$ **1** and $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$[dmdcnqi] **2** were collected at 295 K with a Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Lattice parameters were obtained from the least-squares refinement of the setting angles of 25 reflections with $\theta > 12°$. Details of the crystallographic data collection and structure refinement are summarised in Table 2.

A total of 1869 (**1**) and 2441 (**2**) reflections were collected by the variable-speed ω–2θ scan method in the 2θ range 3–46°; 1779 (**1**) and 2354 (**2**) were unique and, from these, 1524 (**1**) and 1800 (**2**) were assumed as observed $[I \geqslant 3\sigma(I)]$ and used for the refinement of the structures. Examination of three standard reflections, monitored every 60 min, showed no evidence for crystal deterioration. Both data sets were corrected for Lorentz-polarisation effects and also for absorption using the ψ-scan method[8] [maximum and minimum transmission factors 0.999, 0.946 (**1**) and 0.999, 0.976 (**2**)].

The structures of compounds **1** and **2** were solved by standard Patterson methods using the program SHELXS 86[9] and subsequently completed by Fourier recycling and refinement using the program SHELX 76.[9] The full-matrix least-squares refinement was based on $|F_o|$. All the non-H atoms were assigned anisotropic thermal parameters. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. The final full-matrix least-squares refinement using the weighting scheme $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ where $g = 0.0001$ (**1**) and 0.0003 (**2**) converged at R and R' values of 0.028 and 0.029 for **1** and 0.051 and 0.048 for **2**. Neutral-atom scattering factors were used with corrections for anomalous dispersion.[10]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/142.

Results and Discussion

Initial attempts to synthesise organometallic electron-transfer salts of *N*,*N*′-dicyano-*p*-benzoquinone diimine were made using the dinuclear sulfido-bridged complex $[Fe_2(cp)_2(\mu\text{-}SEt)_2(CO)_2]$ as the donor. However, it was apparent that this complex is not sufficiently electron-rich to ensure complete electron transfer in its reactions with the electron-acceptor molecule, as confirmed by cyclic voltammetric measurements, with the result that the product tends to disproportionate to the starting materials or simply to decompose. It was thus decided to employ the pentamethylcyclopentadienyl analogue $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$ **1** as the donor in electron-transfer reactions with a range of dicyano-*p*-benzoquinone diimines. This compound is more electron-rich than the cyclopentadienyl species and, moreover, there is evidence that methyl substitution of the

Table 1 Infrared spectroscopic data (cm^{-1})

Compound	Medium	
	CH_2Cl_2	KBr
1 [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$]	1916s, 1890w (sh)	1918s, 1892m, 1886m, 1854w
2 [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$][dmdcnqi]	2120m, 2092m, 1983s, 1946w	2120ms, 2092ms, 1967s, 1926ms
3 [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$][cmdcnqi]	2127m, 2120m, 2110m, 1984s, 1949mw	2122m, 2108m, 1967s, 1936m
4 [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$][mdcnqi]	2128mw, 2104m, 1983s, 1946mw	2120m, 2096m, 1967s, 1930ms
5 [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$][dcnqi]	2164w, 2124mw, 2098m, 1984s, 1947mw	2160w, 2124mw, 2092m, 1978s, 1946ms

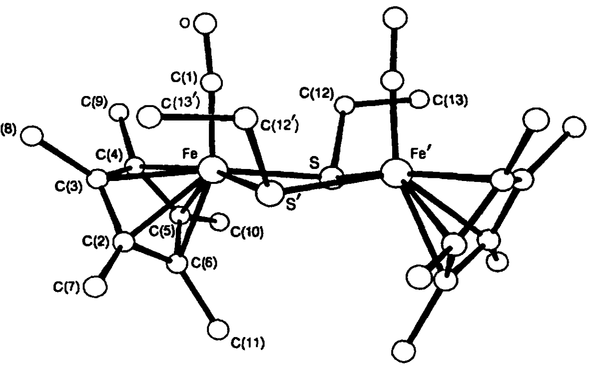

Fig. 1 Perspective view of [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] **1**. Hydrogen atoms are omitted for clarity

Table 2 Crystallographic data for [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] **1** and [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$][dmdcnqi] **2***

	1	**2**
Formula	$C_{26}H_{40}Fe_2O_2S_2$	$C_{36}H_{48}Fe_2N_4O_2S_2$
M	560.41	744.62
a/Å	15.071(3)	18.391(2)
b/Å	14.527(2)	12.978(1)
c/Å	13.024(1)	18.436(2)
β/°	103.74(1)	121.02(7)
U/Å^3	2767(1)	3771(1)
D_c/g cm^{-3}	1.34	1.31
F(000)	1184	1568
Crystal size/mm	0.35 × 0.15 × 0.19	0.27 × 0.23 × 0.06
μ(Mo-Kα)/cm^{-1}	12.34	9.32
R	0.028	0.051
R′	0.029	0.048
Maximum shift/error	0.097	0.069
Maximum difference peak/e Å^{-3}	0.19	0.59

* Details in common: monoclinic, space group *C*2/*c*; $Z = 4$; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}F_o$.

Table 3 Selected interatomic distances (Å) and angles (°) for [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] **1**

Fe • • • Fe′	3.445(1)	Fe–S	2.278(1)
Fe–S′	2.777(1)	Fe–C(1)	1.736(4)
Fe–C(2)	2.121(3)	Fe–C(3)	2.096(3)
Fe–C(4)	2.091(4)	Fe–C(5)	2.105(3)
Fe–C(6)	2.106(3)	C(1)–O	1.155(4)
S–C(12)	1.836(3)		
S–Fe–S′	80.1(1)	S–Fe–C(1)	96.8(1)
S–Fe–Cp	124.2(2)	S′–Fe–C(1)	94.8(2)
S′–Fe–Cp	127.0(2)	C(1)–Fe–Cp	122.9(2)
Fe–S–Fe′	98.3(1)	Fe–S–C(12)	105.8(1)
Fe′–S–C(12)	111.3(3)		

Cp denotes the midpoint of the C_5Me_5 ring.

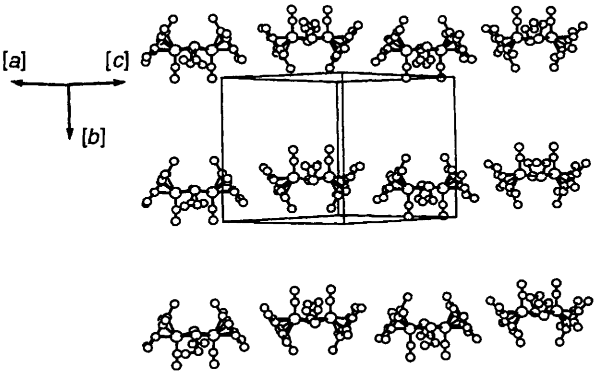

Fig. 2 Stacking of [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] molecules in crystals of compound **1**. Hydrogen atoms are omitted for clarity

cyclopentadienyl rings imparts stability to decamethylmetallocenium ions.[11] The preparation of **1** has not been reported previously and is therefore described together with its crystal structure.

Synthesis and crystal structure of [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] 1

Treatment of the carbonyl ligand-bridged dimer [Fe_2(η-C_5Me_5)$_2$(μ-CO)$_2$(CO)$_2$][12] with an excess of the dialkyl disulfide, Et_2S_2, in toluene under reflux afforded [Fe_2(η-C_5Me_5)$_2$(μ-SEt)$_2$(CO)$_2$] **1** in good yield. The compound was isolated as a brown-black air-stable crystalline material. The infrared spectrum of **1** (Table 1) shows two peaks in the ν(CO) region, at 1916s and 1890 (sh) cm^{-1} measured in dichloromethane, indicative of the presence of terminal carbonyls only in an electron-rich complex. The ^{1}H NMR spectrum measured at room temperature in C_6D_6 exhibits a single peak at δ 1.79 corresponding to the methyl protons of the C_5Me_5 ligands, as well as the expected pattern of a triplet and quartet assigned to the ethyl groups of the bridging EtS ligands. These spectroscopic data are consistent with the presence in solution of both *cis* and *trans* isomers that interconvert at a rate which is fast on the time-scale of the NMR experiment or, alternatively, of only one isomer, presumably the *cis* since this is the isomer present in the solid state as confirmed X-ray crystallographically (see below).

Single crystals of compound **1** were grown by slow cooling of a saturated solution in light petroleum. The crystal structure consists of four dimer molecules in the unit cell of space group *C*2/*c*; thus each dimer molecule possesses a crystallographically imposed C_2 axis. Fig. 1 illustrates the structure of the molecule as well as the atom numbering scheme; selected bonding parameters are listed in Table 3. The molecule comprises two crystallographically identical Fe(C_5Me_5)(CO) units linked to each other by two bridging EtS ligands. The bulky pentamethylcyclopentadienyl ligands are arranged in a *cis* configuration with respect to the Fe–Fe vector, the dihedral angle between the planes of the rings being 62°. This is contrary to what might be expected on purely steric grounds although the same configuration is observed for the cyclopentadienyl ligands in the closely related PhS-bridged complex [Fe_2(cp)$_2$(μ-SPh)$_2$(CO)$_2$].[13] A further consequence of the presence of the C_2 axis is that the S–C bonds are arranged in a *syn* conformation with respect to the S–S vector. The Fe_2S_2 quadrangle in **1** is slightly puckered, the dihedral angle between the planes defined by the two bridging S atoms and one Fe atom being 162°, similar to the equivalent angles of 161 and 164° reported for the two crystallographically independent molecules present in crystals of the benzenethiolate compound.[13] The Fe ··· Fe distance in **1** of 3.445(1) Å is slightly longer than that of 3.39 Å reported for $[Fe_2(cp)_2(\mu\text{-}SPh)_2(CO)_2]$.[13] This distance is consistent with no direct bonding interaction between the iron atoms, as predicted by a simple electron count, *i.e.* a closed-shell configuration is achieved for each iron atom, without the necessity for a Fe–Fe bonding interaction. The Fe–S distances of 2.777(1) and 2.278(1) Å as well as the Fe–S–Fe′ and S–Fe–S′ angles of 98.3(1) and 80.1(1)° are in good agreement with the values of 2.262(6) Å, 98 and 81° respectively reported for the equivalent parameters in $[Fe_2(cp)_2(\mu\text{-}SPh)_2(CO)_2]$.[13] The Fe–C ($C_5Me_5$) distances range from 2.091(4) to 2.121(3) Å, slightly longer than the average Fe–C distance of 2.050(2) Å observed for decamethylferrocene itself.[14]

A view of the packing of the dimer molecules in crystals of **1** is given in Fig. 2. The molecules stack in parallel linear rows or chains which make an angle of *ca.* 50° to the [*c*] axis. The stacking is such that the C_5Me_5 ligands of adjacent molecules are arranged face-to-face with the Fe–C (O) bonds of adjacent molecules pointing in opposite directions. By virtue of the presence of a crystallographic centre of inversion between each successive molecule in the row, the adjacent rings are necessarily parallel. The interplanar distance between the planes defined by the C atoms of adjacent C_5Me_5 ligands is 3.65 Å, a value close to the upper distance limit for π–π interactions in organic species of about 3.8 Å.[15] Indeed, all the intermolecular non-bonded contacts in the crystal are typical of those for a molecular crystal held together by weak van der Waals forces. Nevertheless, the packing motif is of relevance to the use of **1** as a donor in the preparation of electron-transfer salts, since a requirement for co-operative magnetic behaviour in the latter is the presence of extended rows of donor cations and planar acceptor anions in the crystal (see below).

Synthesis and characterisation of $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2][A]$ (A = dcnqi, dmdcnqi, cmdcnqi or mdcnqi)

In order to establish the thermodynamic feasibility of the electron-transfer reactions between the donor **1** and the dicyano-*p*-benzoquinone diimine (dcnqi) acceptor molecules their redox chemistry was investigated by means of cyclic voltammetric measurements in dichloromethane (0.1 mol dm^{-3} NBu_4ClO_4) at a platinum electrode and at a scan rate of 200 mV s^{-1}. Potentials are quoted relative to a pseudo-Ag–AgCl reference electrode. The neutral donor **1** is reversibly oxidised to the cation at a potential $E_{\frac{1}{2}} = -0.27$ V and to the dication at $E_{\frac{1}{2}} = 0.47$ V. The dicyano-*p*-benzoquinone diimines are reversibly reduced in successive one-electron steps as reported by Aumüller and Hünig,[16] but under different experimental conditions. Half-wave potentials obtained by us for the dcnqi–dcnqi$^-$ and dcnqi$^-$–dcnqi^{2-} couples respectively are (in V): 0.14 and −0.49 (dcnqi); 0.08 and −0.51 (dmdcnqi); 0.22 and −0.41 (cmdcnqi); 0.12 and −0.55 (mdcnqi). The potentials for the first reduction are substantially anodic (by at least 0.35 V) of the $E_{\frac{1}{2}}$ value for the $\mathbf{1}^+$–$\mathbf{1}$ couple. Complete electron transfer is therefore expected in the reaction between **1** and the various dicyano-*p*-benzoquinone diimines.[17] On the other hand the potentials for the second reduction of the acceptor molecules are cathodic of that for the donor couple, implying that reduction of the acceptor molecule by **1** will be to the monoanion only. Also, the half-wave potentials for the dcnqi–dcnqi$^-$ couples are cathodic of the $E_{\frac{1}{2}}$ value for the $\mathbf{1}^{2+}$–$\mathbf{1}^+$ couple suggesting that dication formation is not favoured. These data lead to the conclusion that 1 : 1 charge-transfer salt formation will take place in the reactions between **1** and the various dicyano-*p*-benzoquinone diimines.

Addition of an equimolar amount of compound **1** dissolved in toluene to a cooled solution of dmdcnqi in toluene resulted in the formation of a green solution, from which the crude product precipitated as the solvent was gradually removed *in vacuo*. Recrystallisation was effected in acetonitrile to afford a blue-black crystalline material which is moderately stable in air. The other dcnqi salts were prepared similarly. Microanalytical data for C, H and N are consistent with the formulation of the compound as a 1 : 1 salt $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2][A]$ (A = dmdcnqi **2**, cmdcnqi **3**, mdcnqi **4** or dcnqi **5**). Infrared data recorded in the solid state are given in Table 1. As expected the ν(CO) bands observed for the donor cations in these salts are shifted by 50–70 cm^{-1} to higher wavenumbers, as compared to those for the neutral donor. A similar shift of *ca.* 50 cm^{-1} is observed for $[Fe_2(cp)_2(\mu\text{-}SMe)_2(CO)_2]$ and the complex cation present in the tetrafluoroborate salt, $[Fe_2(cp)_2(\mu\text{-}SMe)_2(CO)_2]BF_4$.[18] As anticipated a shift of *ca.* 70 cm^{-1} to lower wavenumbers for the ν(CN) peaks of the acceptor anions as compared to those of the corresponding neutral dicyano-*p*-benzoquinone diimine is also observed. For example, the C–N stretching mode for neutral dmdcnqi occurs at 2168 cm^{-1} in its solid-state infrared spectrum,[6] while two peaks at 2120 and 2092 cm^{-1} are observed in the ν(CN) region of the corresponding spectrum of $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$[dmdcnqi].

Crystal structure and magnetic properties of $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$[dmdcnqi] 2

Single crystals of compound **2** were grown by slow cooling of a saturated solution in acetonitrile. Like the neutral donor molecule **1**, the 1 : 1 salt **2** crystallises in the space group *C*2/*c* with four formula units per unit cell. The cation possesses a crystallographically imposed C_2 axis while the anion is situated on a centre of inversion located at the centroid of the quinone ring. Fig. 3 illustrates the structure and atom-numbering scheme of the cation, and Fig. 4 that of the anion. Table 4 lists the important interatomic distances and angles. The overall stereochemistry of the $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]^{\bullet+}$ cation is in every respect the same as that for the neutral molecule (see above). The dihedral angle between the planes of the C_5Me_5 rings is 68° as compared to 62° in **1**. As observed in **1**, the Fe_2S_2 quadrangle is only slightly puckered, the angle between the planes defined by the two S atoms and each Fe atom being 172°. However, there is a large decrease in the Fe ··· Fe distance from 3.445(1) Å in **1** to 3.083(2) Å in the cation of **2**. This is accompanied by a decrease in the Fe–S–Fe′ angle from 98.3(1)° in **1** to 86.3(1)° in the cation, and a concomitant increase in the S–Fe–S′ angle from 80.1(1)° in the neutral species to 93.4(1)° in the cation. Similar differences in geometry associated with a decrease in the Fe ··· Fe distance (by 0.46 Å) exist between $[Fe_2(cp)_2(\mu\text{-}SPh)_2(CO)_2]$[13] and the $[Fe_2(cp)_2(\mu\text{-}SMe)_2(CO)_2]^{\bullet+}$ cation.[18]

These decreases in the Fe ··· Fe distances associated with the oxidation of species of the type $[Fe_2(cp)_2(\mu\text{-}SR)_2(CO)_2]$ (R =

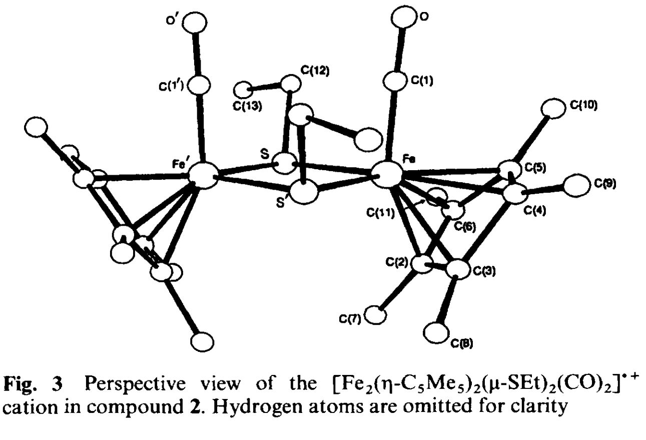

Fig. 3 Perspective view of the $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]^{\bullet+}$ cation in compound **2**. Hydrogen atoms are omitted for clarity

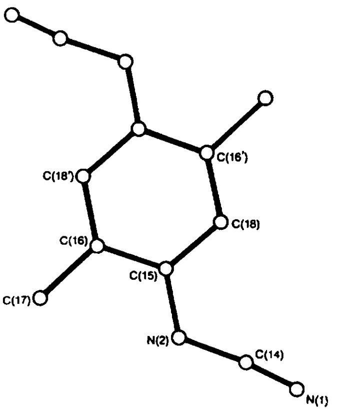

Fig. 4 Perspective view of the [dmdcnqi]$^{\bullet -}$ anion in compound **2**. Hydrogen atoms are omitted for clarity

Table 4 Selected interatomic distances (Å) and angles (°) for [$Fe_2(\eta$-$C_5Me_5)_2(\mu$-$SEt)_2(CO)_2$][dmdcnqi] **2**

Cation			
Fe ··· Fe'	3.083(2)	Fe–S	2.257(2)
Fe–S'	2.250(2)	Fe–C(1)	1.737(7)
Fe–C(2)	2.158(6)	Fe–C(3)	2.164(6)
Fe–C(4)	2.107(6)	Fe–C(5)	2.121(5)
Fe–C(6)	2.135(6)	C(1)–O	1.158(7)
S–C(12)	1.838(6)		
S–Fe–S'	93.4(1)	S–Fe–C(1)	95.3(2)
S–Fe–Cp	120.1(2)	S'–Fe–C(1)	94.7(2)
S'–Fe–Cp	123.8(2)	C(1)–Fe–Cp	122.1(2)
Fe–S–Fe'	86.3(1)	Fe–S–C(12)	108.9(3)
Fe'–S–C(12)	115.1(3)		
Anion			
N(1)–C(14)	1.109(10)	N(2)–C(14)	1.361(11)
N(2)–C(15)	1.348(8)	C(15)–C(16)	1.426(9)
C(15)–C(18')	1.430(9)	C(16)–C(17)	1.515(8)
C(16)–C(18)	1.356(9)		

Cp denotes the midpoint of the C_5Me_5 ring.

alkyl or aryl group) are readily explained by reference to a bonding scheme developed by Mason and Mingos[19] for dinuclear systems containing an $M_2(\mu$-$X)_2$ moiety (M = metal, X = bridging ligand). In terms of this scheme, the highest occupied molecular orbital (HOMO) of the neutral complex is strongly antibonding with respect to the Fe ··· Fe bond, and thus the one-electron oxidation of the complex is expected to lead to an increase in the Fe ··· Fe bond order and a decrease in the Fe ··· Fe distance. The large decrease in the Fe ··· Fe distance on oxidation of **1** by the dicyano-*p*-benzoquinone diimine also implies that complete electron transfer has occurred in this reaction. Comparisons of the bond lengths in neutral dicyano-*p*-benzoquinone diimines with those in the corresponding reduced species may also be used to estimate the charge on the anion, and hence the extent of electron transfer. The bond lengths and angles observed for the dmdcnqi anion in **2** are in good agreement with those reported for the same anion in [ttf][dcnqi]·$2H_2O$[20] [ttf = tetrathiafulvalene; 2-(1,3-dithiol-2-ylidene)-1,3-dithiole] and [Cu(dmdcnqi)$_2$].[21] However, significant differences in these bond lengths compared to those reported for the neutral dmdcnqi molecule[22] are not discernible, largely because of the relatively high standard errors associated with the C–C and C–N distances in **2**.

Fig. 5 illustrates the packing of the [$Fe_2(\eta$-$C_5Me_5)_2(\mu$-$SEt)_2(CO)_2$]$^{\bullet +}$ cations and [dmdcnqi]$^{\bullet -}$ anions in crystals of compound **2**. The dinuclear cations are arranged in parallel rows in a manner entirely analogous to that observed for the packing of the neutral donor molecules in crystals of **1** (Fig. 2); in the case of the salt these rows make an angle of *ca.* 28° to the [*a*] axis. The planar acceptor anions are neatly sandwiched between the C_5Me_5 ligands of neighbouring cations within these rows. Thus the following sequence of donor radical cations ($D^{\bullet +}$) and acceptor radical anions ($A^{\bullet -}$) occurs along the rows: ··· $D^{\bullet +}A^{\bullet -}D^{\bullet +}A^{\bullet -}D^{\bullet +}A^{\bullet -}$ ···. As noted, the anion is positioned on a centre of inversion with the result that the C_5Me_5 rings on either side of any one anion in a row are parallel. However, the mean plane defined by the atoms of the [dmdcnqi]$^{\bullet -}$ anion is orientated at an angle of 11.4° to that defined by the atoms of the C_5Me_5 rings. This would appear to limit the extent of any π–π interactions within the C_5Me_5, [dmdcnqi]$^{\bullet -}$, C_5Me_5 arrangement. On the other hand, the averaged perpendicular distance of the constituent atoms of the [dmdcnqi]$^{\bullet -}$ anion to the planes of the C_5Me_5 rings is *ca.* 3.2 Å, a value which is regarded as optimal for π–π interactions.[15] Fig. 6 gives a view of the C_5Me_5, [dmdcnqi]$^{\bullet -}$, C_5Me_5 arrangement projected onto a plane parallel to that of the anion. This reveals that there is no direct overlap of the C_5Me_5 ligands with the quinone ring or the exocyclic C=N bond of the [dmdcnqi]$^-$ anion, as would be expected for a conventional π–π interaction. Instead, the C_5Me_5 rings are slipped with respect to the anion such that they are positioned directly above and below the C≡N groups of it. Thus, if extended interactions were to occur along the rows of radical cations and anions, communication would have to be *via* overlap of the π orbitals on the cyano groups with those on the pentamethylcyclopentadienyl rings.

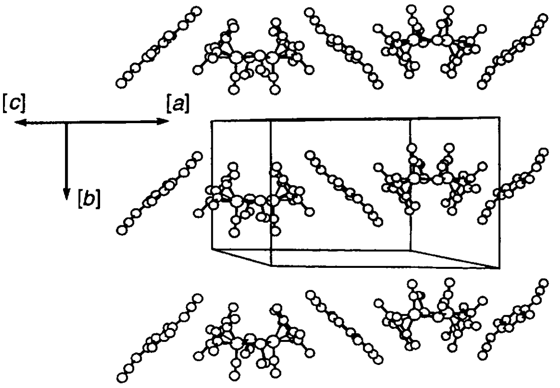

Fig. 5 Stacking of [$Fe_2(\eta$-$C_5Me_5)_2(\mu$-$SEt)_2(CO)_2$]$^{\bullet +}$ cations and [dmdcnqi]$^{\bullet -}$ anions in crystals of compound **2**. Hydrogen atoms are omitted for clarity

The temperature dependence (2–230 K) of the magnetic susceptibility of compound **2** has been measured by the Faraday method,[23] and found to obey the Curie–Weiss law. A plot of the inverse molar susceptibility *versus* temperature displays no obvious deviations from linearity at low temperatures, as would be expected if significant coupling between the unpaired electron spin density on the donor and acceptor ions was present. The Curie–Weiss constant, θ, of 0.414 K is substantially smaller than that typically associated with ferromagnetic coupling, *e.g.* θ = 16.8 K for [$Fe(\eta$-$C_5Me_5)_2$][tcne].[3] It is, however, very similar to the values of θ = 0.5 ± 2.2 K reported for [$Fe(C_5Me_4$-$H)_2$][BF_4] which has been suggested to be indicative of very weak magnetic interactions.[24] The room-temperature effective magnetic moment of 2.72 μ_B is significantly greater than the spin-only value of 2.45 μ_B predicted for two independent non-interacting spins. Presumably this difference arises as a result of orbital angular-momentum contributions to the magnetic moment of **2**, given that extended interactions between the spins do not take place (see below).

The structural motif found in crystals of the electron-transfer salt **2**, *viz.* extended rows of alternating donor radical cations and acceptor radical anions, is the same as that observed in [$Fe(\eta$-$C_5Me_5)_2$][tcne][3] and [$Mn(\eta$-$C_5Me_5)_2$][tcnq][4] both of which demonstrate co-operative magnetic behaviour as

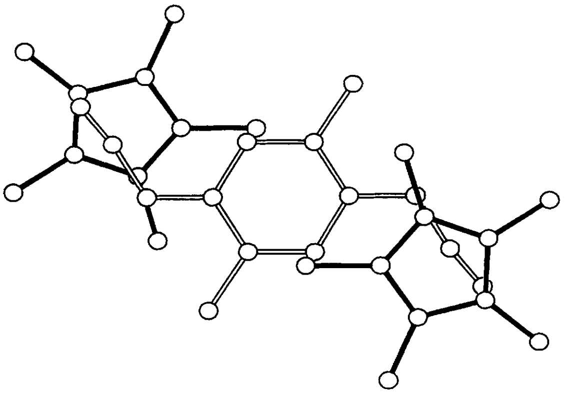

Fig. 6 View perpendicular to the anion plane of the C_5Me_5, $[dmdcnqi]^{\bullet -}$, C_5Me_5 arrangement in crystals of compound **2**. Hydrogen atoms are omitted for clarity

evidenced by Curie–Weiss constants of 16.8 and 10.5 K respectively. The electron-transfer salt $[Fe(\eta\text{-}C_5Me_5)_2][dmdcnqi]$ similarly exhibits ferromagnetic coupling with θ = 10.8 K, though no crystal structure was reported of this compound; indeed the crystal structure of **2** is the first reported of an electron-transfer salt formed from the reaction of an organometallic donor with a dicyanoquinone diimine. Also, the available evidence suggests that complete electron transfer has taken place in the reaction between the dinuclear organometallic donor and the dicyano-*p*-benzoquinone diimine acceptor molecule, *i.e.* each of the cations and anions has a spin $S = \frac{1}{2}$. The question then arises as to why no co-operative magnetic behaviour is observed for **2**. We first note that the detailed packing of the dinuclear donor cations and dmdcnqi acceptor anions is necessarily different from that in the mononuclear metallocenium-based electron-transfer salts such as $[Fe(\eta\text{-}C_5Me_5)_2]^{\bullet +}[tcne]^{\bullet -}$ [3] and $[Mn(\eta\text{-}C_5Me_5)_2]^{2\bullet +}[tcnq]^{\bullet -}$.[4] For instance, the iron atoms of successive dinuclear cations do not all lie on the same stacking axis but rather are disposed on either side of it; this contrasts the situation in the ferrocenium and manganocenium salts where the metal atoms do form a chain. Secondly and probably more importantly, the spin density on the larger dinuclear radical cation, $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]^{\bullet +}$, is less than that on mononuclear metallocenium donor cations such as $[Fe(\eta\text{-}C_5Me_5)_2]^{\bullet +}$ and $[Mn(\eta\text{-}C_5Me_5)_2]^{2\bullet +}$. As noted by Miller and co-workers,[1] higher spin densities on the radical cations and anions favour co-operative magnetic behaviour; the unpaired spin on the radical cation is probably shielded to such an extent that spin–spin interactions with the neighbouring anions are negligible.

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