Synthesis, structural and magnetic characterisation of the electron-transfer salts [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$_2$[tcnq]$_2$ and [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$][tcne] (tcnq = 7,7,8,8-tetracyanoquinodimethane; tcne = tetracyanoethylene) †

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Reaction of the electron-rich thiolate-bridged complex [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$] with 1 molar equivalent of the electron-acceptor compounds 7,7,8,8-tetracyanoquinodimethane (tcnq) and tetracyanoethylene (tcne) is accompanied by electron transfer and resulted in the formation of the dark green crystalline salts [Fe$_2$(η-C$_5$Me$_5$)$_2$-(μ-SEt)$_2$(CO)$_2$]$_2$[tcnq]$_2$ **1** and [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$][tcne] **2** respectively. The crystal structures of these salts have been determined by X-ray diffraction methods and the cations thereof established to have very similar stereochemistries. The C$_5$Me$_5$ ligands are *cis* disposed with respect to the Fe · · · Fe vector with the dihedral angles between their planes being 71 and 68° for **1** and **2** respectively. The Fe · · · Fe distances are respectively 3.077(2) and 3.069(2) Å. Crystals of **1** consist of isolated units of composition D$^{·+}$(A)$_2^{2-}$D$^{·+}$ where D$^{·+}$ denotes the cation and (A)$_2^{2-}$ a (tcnq)$_2^{2-}$ dimer, the planes of the tcnq moieties comprising the dimer and those of the adjacent C$_5$Me$_5$ rings being virtually parallel. The compound is paramagnetic. Crystals of **2** consist of parallel rows of cations and tcne$^{·-}$ anions in the sequence · · · D$^{·+}$A$_A^{·-}$D$^{·+}$A$_B^{·-}$D$^{·+}$A$_A^{·-}$D$^{·+}$A$_B^{·-}$ · · · , where A$_A^{·-}$ and A$_B^{·-}$ label crystallographically independent anions. The two types of tcne$^{·-}$ anion are themselves approximately planar, but define different angles to the planes of the adjacent C$_5$Me$_5$ rings of 4 and 72°. Magnetic susceptibility measurements for **2**, in the range 5.0 to 310.0 K, suggest very little magnetic coupling between the unpaired spins on the cations and the tcne$^{·-}$ anions and thus this compound is also paramagnetic.

Ferrocene and its derivatives have been used extensively as donors in electron-transfer reactions with acceptor compounds such as 7,7,8,8-tetracyanoquinodimethane (tcnq) and tetracyanoethylene (tcne). Decamethylferrocene, for example, has been shown to react with tcnq to afford a 1:1 paramagnetic salt[1] and a 1:1 metamagnetic salt.[2] Crystals of the 1:1 paramagnetic salt consist of isolated units of composition Fe-(η-C$_5$Me$_5$)$_2$/tcnq/tcnq/Fe(η-C$_5$Me$_5$)$_2$ in which the 'acceptor' anions are present as strongly antiferromagnetically coupled (tcnq)$_2^{2-}$ dimers.[1] This compound is thus formulated as [Fe(η-C$_5$Me$_5$)$_2$]$_2$[tcnq]$_2$, the origin of the paramagnetism being the isolated spins on the decamethylferrocenium cations. The structural motif in the metamagnetic salt is one of a row of alternating cations and anions, *i.e.* · · · D$^{·+}$A$^{·-}$D$^{·+}$A$^{·-}$ · · · where D$^{·+}$ denotes the cation and A$^{·-}$ the tcnq$^{·-}$ anion.[3] This salt has a Curie–Weiss constant θ of 12.3 K and a critical temperature T_c of 2.55 K. The 1:1 [Fe(η-C$_5$Me$_5$)$_2$][tcne] salt has also been prepared and shown to have the same · · · D$^{·+}$A$^{·-}$D$^{·+}$A$^{·-}$ · · · motif.[4] The Curie–Weiss constant θ for this salt is 16.8 K while the critical temperature T_c is 4.8 K; the salt behaves as a bulk ferromagnet at temperatures below 4.8 K and as such was the first molecular material to be reported which exhibits bulk ferromagnetic behaviour below its critical temperature.[5] Other metallocene donors such as manganocene and chromocene have also been treated with tcne and found to give 1:1 electron-transfer salts all of which have in common the · · · D$^{·+}$A$^{·-}$D$^{·+}$A$^{·-}$ · · · structural motif; these salts generally exhibit co-operative magnetic phenomena.[6]

We have embarked on a programme involving the use of dinuclear organometallic compounds, in particular ligand-bridged dinuclear systems, as donors in electron-transfer reactions with planar polycyanohydrocarbon electron-acceptor compounds. One particular complex we have investigated in this context is the electron-rich diphosphazane ligand-bridged dimer [Fe$_2$(η-C$_5$H$_5$)$_2$(μ-CO)$_2${μ-Ph$_2$PN(Et)PPh$_2$}]. With tcnq this dinuclear species was shown to afford the 2:3 salt [Fe$_2$(η-C$_5$H$_5$)$_2$(μ-CO)$_2${μ-Ph$_2$PN(Et)PPh$_2$}]$_2$[tcnq]$_3$·2MeCN, as confirmed X-ray crystallographically,[7] while with tcne it gave the 1:1 salt [Fe$_2$(η-C$_5$H$_5$)$_2$(μ-CO)$_2${μ-Ph$_2$PN(Et)PPh$_2$}][tcne]. More recently, we have employed the thiolate-bridged dimer [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$] as the donor in electron-transfer reactions with acceptor compounds of this type. The results of its reactions with tcnq and tcne are reported here; those of its reactions with *N,N*-dicyanoquinone diimines together with the crystal structure and magnetic properties of [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]-[dmdcnqi] (dmdcnqi = *N,N*-dicyano-2,5-dimethyl-*p*-benzoquinone diimine), in particular, are given in a separate paper.[8]

Experimental

Syntheses

[Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$_2$[tcnq]$_2$ 1. A solution of [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$] (0.056 g, 0.100 mmol) in toluene

(10 cm³) was added dropwise over *ca.* 10 min to a stirred solution of tcnq (0.018 g, 0.088 mmol) in acetonitrile–toluene (1:4, 5 cm³) at room temperature. On completion of the addition the volume of the reaction mixture was reduced *in vacuo*, resulting in the separation of the product as a dark green microcrystalline powder. It was filtered off, washed with light petroleum (b.p. 60–80 °C) and dried *in vacuo*. Yield *ca.* 0.057 g, 75% (Found: C, 59.1; H, 5.9; N, 7.25. $C_{76}H_{88}Fe_4N_8O_4S_4$ requires C, 59.7; H, 5.8; N, 7.35%). IR (KBr): ν(CO) 1978s, 1941w (sh); ν(CN) 2178s, 2156m cm^{-1}.

[Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂][tcne] 2. A solution of tcne (0.017 g, 0.133 mmol) in toluene (7 cm³) was added dropwise over *ca.* 20 min to a stirred solution of [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂] (0.079 g, 0.141 mmol) in toluene (10 cm³) at room temperature. The product which separated as a dark green microcrystalline solid was filtered off, washed in sequence with toluene and diethyl ether and dried *in vacuo*. Yield *ca.* 0.072 g, 80% (Found: C, 55.8; H, 5.8; N, 7.9. $C_{32}H_{40}Fe_2N_4O_2S_2$ requires C, 55.8; H, 5.85; N, 8.15%). IR (KBr): ν(CO) 1978s, 1946 (sh); ν(CN) 2188w, 2148m cm^{-1}.

Electrochemical procedures

Cyclic voltammograms were recorded using a PAR 175 universal programmer, a PAR 173 potentiostat fitted with a PAR 176 current follower connected to a HP 7045A X-Y recorder. All measurements were carried out under argon in acetonitrile. The solvent was purified by refluxing over phosphorus pentaoxide, followed by at least two fractional distillations through a metre-long vacuum-jacketed glass helix column. The salt NBu₄ClO₄ was purified by repeated crystallisations from ethanol–water mixtures and dried at 80 °C under a 10 mmHg vacuum. Compound concentrations were 0.001 ± 0.0001 mol dm^{-3}. All the experiments employed a conventional three-electrode configuration comprising a platinum-disc working electrode (0.013 cm²), a platinum-spiral wire auxiliary electrode and a reference electrode comprising a AgCl-coated silver wire dipped in a 0.1 mol dm^{-3} solution of NBu₄ClO₄ in acetonitrile and separated from the electrolyte solution by a fine frit. Ferrocene was added to the solution under investigation at the end of each experiment as an internal standard to check on the stability of the reference electrode. Measurements were made at 25 ± 2 °C.

Crystallography

Crystals of complex **1** were grown by cooling a solution of the salt in acetonitrile–toluene (1:1) overnight at −6 °C; crystals of **2** were grown similarly except that the mixture was cooled to −20 °C and left to stand for 2 weeks. Diffractometer data for [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂]₂[tcnq]₂ **1** and [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂][tcne] **2** were collected at 295 K with a Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). Lattice parameters were obtained from the least-squares refinement of the setting angles of 25 reflections with $\theta > 12°$. The crystallographic data collection and structure refinement are summarised in Table 1.

A total of 4894 (complex **1**) and 3837 (**2**) reflections were collected by the variable-speed ω–2θ scan method in the range $3 \leqslant 2\theta \leqslant 46°$; 4774 (**1**) and 3699 (**2**) were unique and, from these, 3531 (**1**) and 2484 (**2**) were assumed as observed $[I \geqslant 3\sigma(I)]$ and used for the refinement of the structures. Examination of three standard reflections, monitored after every 60 min, showed no evidence for crystal deterioration. Both data sets were corrected for Lorentz-polarisation effects and were also corrected for absorption using the φ-scan method[10] [maximum and minimum transmission factors are 0.999, 0.954 (**1**) and 0.999, 0.966 (**2**)].

The structures were solved by standard Patterson methods using the program SHELXS 86[11] and subsequently completed by Fourier recycling and refinement using the program SHELX

76.[11] The full-matrix least-squares refinement was based on $|F_o|$. All non-hydrogen atoms were assigned anisotropic thermal parameters. 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 $g = 0.0033$ (**1**) and 0.0003 (**2**) converged at R and R' values of 0.042 and 0.049 for **1** and 0.044 and 0.041 for **2**. The number of parameters refined for structures **1** and **2** were 470 and 416 respectively. Neutral-atom scattering factors were used with corrections for anomalous dispersion.[12]

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.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/524.
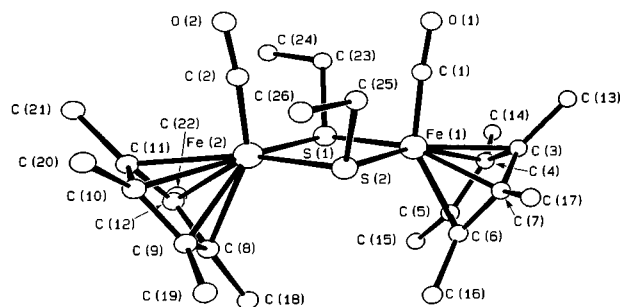
Results and Discussion

In order to establish the thermodynamic feasibility of the electron-transfer reactions between [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂] and either 7,7,8,8-tetracyanoquinodimethane (tcnq) or tetracyanoethylene (tcne) their redox chemistry was investigated. This was achieved by means of cyclic voltammetric measurements in dichloromethane (0.1 mol dm^{-3} NBu₄ClO₄) at a platinum electrode and at a scan rate of 200 mV s^{-1}; potentials are quoted relative to the ferrocene–ferrocenium couple. The neutral donor **1** is reversibly oxidised to the cation at a potential $E_{\frac{1}{2}} = -0.71$ V and to the dication at $E_{\frac{1}{2}} = 0.03$ V. Both tcnq and tcne are reversibly reduced in successive one-electron steps the half-wave potentials being −0.30 and −0.88 V (tcnq) and −0.23 and −1.29 V (tcne). On the basis of the potential data it can be concluded that both tcnq and tcne will undergo a one-electron reduction on reaction with [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂]. Treatment of a toluene solution of tcnq with a *ca.* 1 molar equivalent of [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂] was found to afford a deep green solution from which [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂]₂[tcnq]₂ **1** could be isolated as a dark green microcrystalline solid. The solid-state infrared spectrum of **1**, recorded as a KBr pellet, exhibits peaks in the C–O stretching region at 1978 cm^{-1} with a shoulder at 1941 cm^{-1}, and in the C–N stretching region at 2178 and 2156 cm^{-1}. As expected the C–O stretching frequencies associated with the [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂]$^{\cdot+}$ cation are shifted to higher wavenumbers compared to those of 1918s and 1890 (sh) cm^{-1} observed for neutral [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂].[8] The C–N stretching frequencies can be used as a guide to the charge on the tcnq moiety and, being in close agreement with those reported for salts known to contain the tcnq$^{\cdot-}$ anion,[13] are consistent with complete one-electron transfer having occurred from the donor to the tcnq acceptor molecule. The tcne salt [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂][tcne] **2** was prepared similarly and was also isolated as a dark green microcrystalline solid. The solid-state infrared spectrum of **2**, recorded as a KBr pellet, exhibits peaks in the ν(CO) region at 1978 cm^{-1} with a shoulder at 1946 cm^{-1} and in the ν(CN) region at 2188 and 2148 cm^{-1}. As anticipated, on the basis that all three salts contain the [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂]$^+$ cation, the C–O stretching frequencies for this salt are very similar to those reported for **1** and as well as those for [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂][dmdcnqi].[8] The C–N stretching frequencies are very similar to those reported for salts containing the tcne$^{\cdot-}$ anion,[13] consistent with the presence of the monoanion in **2**.

Structural and magnetic characterisation of [Fe₂(η-C₅Me₅)₂-(μ-SEt)₂(CO)₂]₂[tcnq]₂ 1

The geometry of the [Fe₂(η-C₅Me₅)₂(μ-SEt)₂(CO)₂]$^{\cdot+}$ cation in **1** and the numbering scheme for the atoms comprising the cation

Table 1 Crystallographic data for [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$_2$-[tcnq]$_2$ **1** and [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$][tcne] **2** respectively

	1	**2**
Formula	C$_{76}$H$_{88}$Fe$_4$N$_8$O$_4$S$_4$	C$_{32}$H$_{40}$Fe$_2$N$_4$O$_2$S$_2$
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2$_1$/n (no. 14)
Z	4	4
M	1528.32	688.51
a/Å	34.406(3)	11.815(3)
b/Å	9.224(1)	19.916(4)
c/Å	25.539(2)	14.535(3)
β/°	111.45(6)	98.56(2)
U/Å^3	7544(1)	3382(1)
D$_c$/g cm^{-3}	1.35	1.35
F(000)	3200	1440
Crystal size/mm	0.28 × 0.16 × 0.19	0.32 × 0.18 × 0.16
μ(Mo-Kα)/cm^{-1}	9.37	10.31
R	0.042	0.044
R'	0.049	0.041
Maximum shift/error	0.124	0.082
Maximum difference peak/e Å^{-3}	0.66	0.41

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}F_o$.

Fig. 1 Perspective view of the [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$^{\cdot+}$ cation in complex **1**

are depicted in Fig. 1. Selected interatomic distances and angles are given in Table 2. The cation can be considered as consisting of two nearly identical Fe(η-C$_5$Me$_5$)(CO) units bridged by two ethylthio ligands. The pentamethylcyclopentadienyl ligands are *cis* disposed with respect to the Fe $\cdots$ Fe vector, as evidenced by a Mp(1)–Fe(1)–Fe(2)–Mp(2) torsion angle of 4.3° (Mp denotes the midpoint of a C$_5$Me$_5$ ring). The dihedral angle between the mean planes through the constituent atoms of the C$_5$Me$_5$ ligands is 71°. The S–C bonds of the ethylthio groups define a *syn* conformation with respect to the S $\cdots$ S vector but, in contrast to that observed for the neutral donor molecule and the dmdcnqi salt,[8] the C–C bonds of the ethyl groups adopt a *syn* rather than an *anti* conformation with respect to the C(23) $\cdots$ C(25) vector. Presumably, these small differences in stereochemistry are a consequence of crystal-packing effects. The Fe$_2$S$_2$ quadrangle in **1** is essentially planar with a dihedral angle between the planes defined by the two bridging S atoms and the one Fe atom of 180°. This is in contrast to the Fe$_2$S$_2$ units in the neutral molecule and in the cation of the dmdcnqi salt, which are slightly puckered, as evidenced by equivalent dihedral angles of 162 and 172° respectively.[8] The Fe $\cdots$ Fe distance in the cation is 3.077(1) Å. This distance is similar to that of 3.083(2) Å for the cation of [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$-(CO)$_2$][dmdcnqi] but is *ca.* 0.37 Å shorter than that for neutral [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$].[8] The shorter Fe $\cdots$ Fe distances in the cations as compared to that in [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$] are consistent with the removal of an electron from a HOMO (highest occupied molecular orbital) of the neutral molecule which is antibonding with respect to the Fe $\cdots$ Fe bond. Indeed, separate molecular orbital calculations by

Table 2 Selected interatomic distances (Å) and angles (°) for [Fe$_2$-(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$_2$[tcnq]$_2$ **1**

Cation

Fe(1) $\cdots$ Fe(2)	3.077(1)	Fe(1)–S(1)	2.235(2)
Fe(1)–S(2)	2.252(1)	Fe(2)–S(1)	2.266(1)
Fe(2)–S(2)	2.255(2)	Fe(1)–C(1)	1.750(6)
Fe(2)–C(2)	1.752(6)	Fe(1)–C(3)	2.135(5)
Fe(1)–C(4)	2.119(5)	Fe(1)–C(5)	2.179(5)
Fe(1)–C(6)	2.164(5)	Fe(1)–C(7)	2.109(5)
Fe(2)–C(8)	2.167(5)	Fe(2)–C(0)	2.158(5)
Fe(2)–C(10)	2.122(5)	Fe(2)–C(11)	2.124(5)
Fe(2)–C(12)	2.145(5)	S(1)–C(23)	1.845(6)
S(2)–C(25)	1.847(5)		

S(1)–Fe(1)–S(2)	94.3(1)	S(1)–Fe(1)–C(1)	93.9(2)
S(1)–Fe(1)–Mp(1)	125.2(2)	S(2)–Fe(1)–C(1)	93.6(2)
S(2)–Fe(1)–Mp(1)	121.7(2)	C(1)–Fe(1)–Mp(1)	120.1(2)
S(1)–Fe(2)–S(2)	193.4(1)	S(1)–Fe(2)–C(2)	94.1(2)
S(1)–Fe(2)–Mp(2)	123.0(2)	S(2)–Fe(2)–C(2)	93.7(2)
S(2)–Fe(2)–Mp(2)	123.3(2)	C(2)–Fe(2)–Mp(2)	121.4(2)
Fe(1)–S(1)–Fe(2)	86.2(1)	Fe(1)–S(2)–Fe(2)	86.1(1)

Anion

N(1)–C(34)	1.140(8)	N(2)–C(35)	1.134(8)
N(3)–C(37)	1.151(8)	N(4)–C(38)	1.150(7)
C(27)–C(28)	1.390(7)	C(28)–C(29)	1.364(7)
C(29)–C(30)	1.425(7)	C(30)–C(31)	1.419(7)
C(31)–C(32)	1.363(7)	C(27)–C(32)	1.435(7)
C(27)–C(33)	1.416(7)	C(33)–C(34)	1.413(8)
C(33)–C(35)	1.420(9)	C(30)–C(36)	1.418(7)
C(36)–C(37)	1.408(9)	C(36)–C(38)	1.427(8)

Mp denotes the midpoint of the C$_5$Me$_5$ ring.

Mason and Mingos[14] and by Teo *et al.*[15] on systems containing a M$_2$(μ-X)$_2$ moiety (M = metal, X = bridging ligand) indicate that the HOMO for the Fe$_2$(μ-SEt)$_2$ unit is expected to be strongly antibonding with respect to the Fe $\cdots$ Fe bond. Furthermore, in terms of their scheme the Fe $\cdots$ Fe bond order in the [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$^{\cdot+}$ cation is one half, *i.e.* consistent with the presence of a 'one-electron metal–metal bond'.[15] The decrease in the Fe $\cdots$ Fe distance on removal of an electron from [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$] is accompanied by a decrease in the Fe–S–Fe angle from 98° in the neutral molecule to an average value of 86° in the cation of **1**, as well as an increase in the S–Fe–S angle from 80° in the neutral molecule[8] to an average value of 94° in the same cation. There is also a small decrease of *ca.* 0.03 Å in the Fe–S distances observed for the cation compared to those found for the neutral molecule; a similar decrease also occurs in the Fe–S distances for the cation of the dmdcnqi salt.[8]

The tcnq$^{\cdot-}$ anion in complex **1** is essentially planar, the maximum deviation of any one atom from the mean plane through the constituent atoms being *ca.* 0.2 Å. Further support for a charge of −1 on the tcnq moiety comes from a comparison of the C–N bond lengths as well as the endocyclic and exocyclic C–C bond lengths with those reported for other salts known to contain the tcnq$^{\cdot-}$ anion; they are very similar to those reported for Rb(tcnq) for example.[16] In fact the tcnq$^{\cdot-}$ anions pack in the crystal as strongly antiferromagnetically coupled (tcnq)$_2^{2-}$ dimers but the formal charge on each tcnq moiety is nonetheless −1. Fig. 2 illustrates the arrangement of the [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$^{\cdot+}$ cations and the (tcnq)$_2^{2-}$ dimers in the crystal. They occur in rows, these rows being at an angle of *ca.* 33° to the a axis. The sequence of cations and anions within any one row is $\cdots$D$^{\cdot+}$(A)$_2^{2-}$D$^{\cdot+}$D$^{\cdot+}$(A)$_2^{2-}$D$^{\cdot+}$D$^{\cdot+}$(A)$_2^{2-}$D$^{\cdot+}$$\cdots$ where D$^{\cdot+}$ denotes the cation of the donor and (A)$_2^{2-}$ the (tcnq)$_2^{2-}$ dimer. Note that each D$^{\cdot+}$(A)$_2^{2-}$D$^{\cdot+}$ unit is isolated from the previous and succeeding one, since the adjacent C$_5$Me$_5$ rings of neighbouring donor cations are virtually perpendicular to each other. The structural motif in crystals of **1** is thus analogous to that reported for the paramagnetic phase of
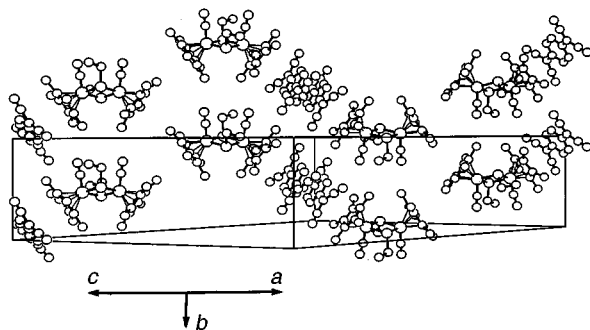
Fig. 2 Packing of $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]^{\cdot+}$ cations and $(tcnq)_2^{2-}$ dimers in crystals of complex **1**

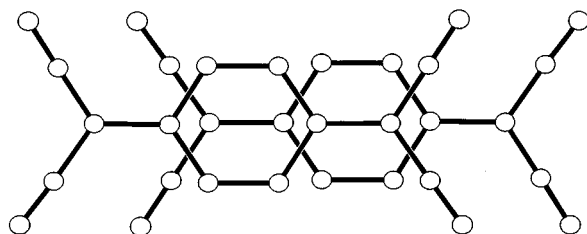**Fig. 3** View of the $(tcnq)_2^{2-}$ dimer perpendicular to the molecular planes

$[Fe(\eta\text{-}C_5Me_5)_2]_2[tcnq]_2$.[1] Within each $D^{\cdot+}(A)_2^{2-}D^{\cdot+}$ unit the planes of the tcnq moieties are necessarily parallel, since there is a crystallographic centre of inversion midway between them. Furthermore, the angle between these planes and those of the adjacent C_5Me_5 rings is only 2°, *i.e.* the C_5Me_5 rings of the cations of the donor and the $tcnq^{\cdot-}$ anions define a face-to-face arrangement within any one $D^{\cdot+}(A)_2^{2-}D^{\cdot+}$ unit. The perpendicular distance between the C_5Me_5 and adjacent tcnq planes is 3.62 Å, a value close to the upper distance limit for π–π interactions in organic species of about 3.8 Å.[17] The implication of this is that any π–π interaction between the C_5Me_5 rings and the tcnq moieties will be weak. On the other hand the perpendicular distance between the tcnq moieties constituting the dimer is 3.262 Å, providing clear evidence for a strong π–π interaction between the two. Indeed, the interplanar spacing is typical of that observed for other salts containing $(tcnq)_2^{2-}$ dimers such as $[Nb_3(\mu\text{-}Cl)_6(C_6Me_6)][tcnq]_2$ (3.10 Å)[18] and the paramagnetic phase of $[Fe(\eta\text{-}C_5Me_5)_2]_2[tcnq]_2$ (3.147 Å).[1] Fig. 3 presents a view of the $(tcnq)_2^{2-}$ dimer perpendicular to the molecular planes. As can be seen the tcnq units are offset along the long molecular axis such that the overlap is of the ring-over-exocyclic double-bond type, the mode of interaction normally observed to occur between tcnq units and indeed established for $[Nb_3(\mu\text{-}Cl)_6(C_6Me_6)][tcnq]_2$.[18] This contrasts the situation for the paramagnetic phase of $[Fe(\eta\text{-}C_5Me_5)_2]_2[tcnq]_2$ in which the offset is along the short molecular axis and the overlap is of the ring–ring type.[1] Nevertheless, this latter salt and **1** have in common the presence of strongly antiferromagnetically coupled $(tcnq)_2^{2-}$ dimers in the crystalline state, with the result that the only unpaired spin is located on the organometallic cation; in terms of the crystal packing described above these spins are too far separated for co-operative magnetic interactions to occur between them. Thus compound **1**, like the decamethylferrocene derivative, is expected to be paramagnetic. That this is the case is supported by a room-temperature effective magnetic moment for **1** of 2.72 μ_B, obtained after corrections for the diamagnetic contributions of both the donor and acceptor anions. This value is somewhat larger than that of 2.45 μ_B predicted using a spin-only approach for non-interacting systems of spin $S=\frac{1}{2}$, presumably because of a contribution from orbital angular momentum to the magnetic moment.
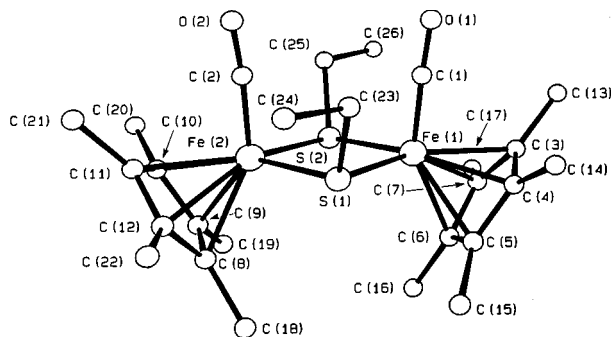

Fig. 4 Perspective view of the $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]^{\cdot+}$ cation in complex **2**

Table 3 Selected interatomic distances (Å) and angles (°) for $[Fe_2\text{-}(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2][tcne]$ **2**

Cation

Fe(1)–Fe(2)	3.069(1)	Fe(1)–S(1)	2.249(2)
Fe(1)–S(2)	2.246(2)	Fe(2)–S(1)	2.253(2)
Fe(2)–S(2)	2.248(2)	Fe(1)–C(1)	1.748(8)
Fe(2)–C(2)	1.758(9)	Fe(1)–C(3)	2.110(7)
Fe(1)–C(4)	2.090(7)	Fe(1)–C(5)	2.163(6)
Fe(1)–C(6)	2.166(7)	Fe(1)–C(7)	2.140(7)
Fe(1)–C(8)	2.150(7)	Fe(2)–C(9)	2.157(7)
Fe(2)–C(10)	2.099(7)	Fe(2)–C(11)	2.119(7)
Fe(2)–C(12)	2.132(7)	S(1)–C(23)	1.840(8)
S(2)–C(25)	1.832(7)		
S(1)–Fe(1)–S(2)	94.0(1)	S(1)–Fe(1)–C(1)	93.2(3)
S(1)–Fe(1)–Mp(1)	122.4(2)	S(2)–Fe(1)–C(1)	94.8(2)
S(2)–Fe(1)–Mp(1)	123.7(2)	C(1)–Fe(1)–Mp(1)	121.0(2)
S(1)–Fe(2)–S(2)	93.8(1)	S(1)–Fe(2)–C(2)	94.3(2)
S(1)–Fe(2)–Mp(2)	123.3(2)	S(2)–Fe(2)–C(2)	94.8(3)
S(2)–Fe(2)–Mp(2)	122.3(2)	C(2)–Fe(2)–Mp(2)	120.8(2)
Fe(1)–S(1)–Fe(2)	85.9(1)	Fe(1)–S(2)–Fe(2)	86.1(1)

Anion A

N(1)–C(28)	1.09(1)	N(2)–C(29)	1.11(1)
C(27)–C(27')	1.04(2)	C(27)–C(28)	1.81(3)
C(27)–C(29)	1.37(2)		

Anion B

N(3)–C(31)	1.11(1)	N(4)–C(32)	1.14(2)
C(30)–C(30')	1.37(2)	C(30)–C(31)	1.42(1)
C(30)–C(32)	1.40(2)		

Mp denotes the midpoint of the C_5Me_5 ring.

Structural and magnetic characterisation of $[Fe_2(\eta\text{-}C_5Me_5)_2\text{-}(\mu\text{-}SEt)_2(CO)_2][tcne]$ **2**

The geometry of the $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]^{\cdot+}$ cation in **2** and the numbering scheme for the atoms comprising the cation are depicted in Fig. 4. Selected interatomic distances and angles are given in Table 3. The stereochemistry of the cation in **2** is very similar to that in **1**. Thus, the pentamethylcyclopentadienyl ligands are *cis* disposed with respect to the Fe $\cdots$ Fe vector, the Mp(1)–Fe(1)–Fe(2)–Mp(2) torsion angle being 2.1°. The dihedral angle between their planes is 68°. The S–C bonds of the ethylthio ligands define a *syn* conformation with respect to the S $\cdots$ S vector, as found for the cation in **1** and for the bridging ligands in neutral $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]$ and the cation in $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2][dmdcnqi]$.[8] Interestingly however, the C–C bonds of the ethyl groups adopt an *anti* conformation with respect to the C(23) $\cdots$ C(25) vector, in contrast to the *syn* conformation observed for **1**, but similar to that found for the neutral molecule and for the cation of the dmdcnqi salt.[8] Clearly, a small difference in the energies of the two conformations has allowed the relative dispositions of the C–C bonds to be determined by crystal-packing forces. The Fe_2S_2
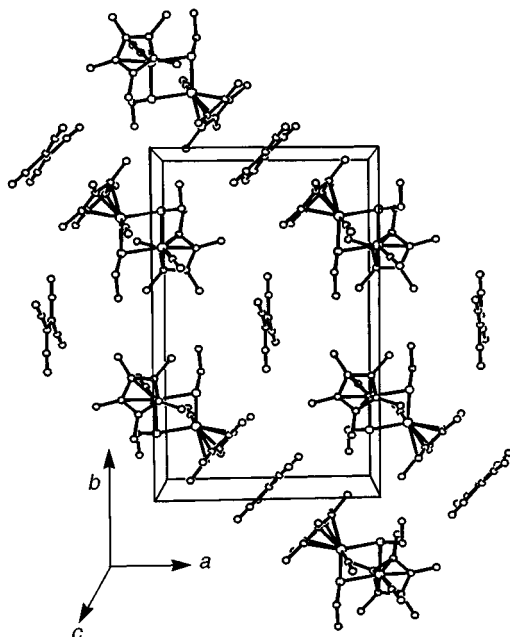
Fig. 5 Packing of [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$^{\cdot +}$ cations and tcne$^{\cdot -}$ anions in crystals of **2**

Fig. 6 Linearised plot of χ_m^{-1} against temperature for [Fe$_2$(η-C$_5$-Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$][tcne] **2**

quadrangle in **2** is slightly puckered, the dihedral angle between the planes defined by the two bridging S atoms and one of the Fe atoms being 177°, a value very similar to the equivalent angles of 172° observed in [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]-[dmdcnqi],[8] but somewhat larger than that of 162° reported for neutral [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$].[8] The Fe · · · Fe distance of 3.069(2) Å for **2** is very similar to the corresponding distances of 3.077(2) and 3.083(2) Å observed for the cations of **1** and the dmdcnqi salt respectively but, as expected, is *ca.* 0.38 Å shorter than the Fe · · · Fe distance observed for the neutral molecule.[8] Also expected is a smaller average Fe–S–Fe angle of 86° and a larger average S–Fe–S angle of 94° compared to those of 98 and 80°, respectively, for the neutral molecule. The Fe–S distances vary between 2.246 and 2.253 Å with an average of 2.248 Å, which is *ca.* 0.03 Å shorter than the Fe–S bond lengths observed for the neutral molecule.[8]

The asymmetric unit in crystals of complex **2** contains two independent tcne half-units, each tcne unit being situated on a crystallographic centre of inversion. Owing to high thermal vibration, the standard errors associated with the bonding parameters are large, particularly for the tcne$^{\cdot -}$ anion labelled A. The tcne$^{\cdot -}$ (B) anion is essentially planar, the maximum deviation of any one atom from the best plane through the constituent atoms being *ca.* 0.05 Å. The A anion shows significant deviations from planarity, these being the consequence of the high thermal motion associated with the atoms comprising this anion, rather than of any inherent non-planarity. Insofar as the C–C and C–N bond lengths in the two anions are concerned, these agree within experimental error with those reported for other salts that contain the tcne$^{\cdot -}$ anion, *e.g.* [Fe(C$_5$Me$_5$)$_2$][tcne].[4] However, the large standard errors in these parameters preclude any attempt to use them as a reliable indication of the charge on the tcne moiety by applying guidelines that have been reported previously.[13] Fig. 5 illustrates the packing of the [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$^{\cdot +}$ cations and tcne$^{\cdot -}$ anions in crystals of **2**. The crystal structure can be described as one of sheets parallel to the *ab* plane, each sheet consisting of rows of donor cations and acceptor anions. The cations and anions alternate along any one row thus defining the sequence · · · D$^{\cdot +}$A$_A$$^{\cdot -}D^{\cdot +}A_B$$^{\cdot -}D^{\cdot +}A_A$$^{\cdot -}D^{\cdot +}A_B$$^{\cdot -}$ · · · where D$^{\cdot +}$ denotes the cation derived from the donor and A$_A$$^{\cdot -}$ and A$_B$$^{\cdot -}$ denote the crystallographically independent tcne$^{\cdot -}$ anions, see above. However, the chains of cations and

anions cannot be described as extended since the plane of a tcne$^{\cdot -}$ (B) anion is not parallel to those of the two adjacent C$_5$Me$_5$ rings, but rather defines an angle of 72° to them. As noted above, the anions are situated on crystallographic centres of inversion and thus the C$_5$Me$_5$ rings on either side of an anion are necessarily parallel. In contrast, the mean plane through the constituent atoms of a tcne$^{\cdot -}$ (A) anion is virtually parallel to those of the two neighbouring C$_5$Me$_5$ rings (dihedral angle = 4°), the averaged perpendicular distance between these planes being *ca.* 3.68 Å. This distance is slightly longer than the equivalent separation of 3.51 Å reported for [Fe(η-C$_5$Me$_5$)$_2$][tcne][4] but less than 3.8 Å, the distance predicted from van der Waals as an upper limit for π-aromatic interactions.[17] In summary, the crystal structure of **2** can be described as comprising isolated D$^{\cdot +}$A$_A$$^{\cdot -}D^{\cdot +}$ units arranged in rows, the rows in turn being arranged in sheets. Within any one such unit the C$_5$Me$_5$ rings and the tcne$^{\cdot -}$ anion participate in a face-to-face arrangement, but these D$^{\cdot +}$A$_A$$^{\cdot -}D^{\cdot +}$ units are separated by tcne$^{\cdot -}$ anions (A$_B$$^{\cdot -}$) which act as spectator ions that preserve the electrical neutrality of the lattice. To the best of our knowledge, compound **2** provides the first example of a metallocene-based electron-transfer salt of tcne that exhibits this structural motif. Generally, compounds of this type crystallise either with extended chains of alternating donor and acceptor ions, *i.e.* · · · D$^{\cdot +}$A$^{\cdot -}$D$^{\cdot +}$A$^{\cdot -}$ · · · as is observed for [Fe(η-C$_5$Me$_5$)$_2$][tcne][4] and [Mn(C$_5$Me$_5$)$_2$][tcne],[19] or with a · · · D$^{\cdot +}$D$^{\cdot +}$(A)$_2$$^{2-}D^{\cdot +}D^{\cdot +}(A)_2$$^{2-}$ · · · arrangement containing the (tcne)$_2$$^{2-}$ anion, as observed for [Cr-(C$_6$H$_6$)$_2$]$_2$[tcne]$_2$.[20]

Unpaired spins are located on the [Fe$_2$(η-C$_5$Me$_5$)$_2$(μ-SEt)$_2$(CO)$_2$]$^{\cdot +}$ cations and tcne$^{\cdot -}$ anions in crystals of complex **2** such that there is the possibility of co-operative magnetic interactions occurring. However, although the structural motif of rows of alternating donor cations and acceptor anions is present in **2**, extended spin–spin interactions along these rows are not anticipated since one of the tcne$^{\cdot -}$ anions does not participate in a face-to-face arrangement with the adjacent C$_5$Me$_5$ rings, see above. This contrasts the situation in crystals of [Fe(η-C$_5$Me$_5$)$_2$][tcne] where the C$_5$Me$_5$ rings and tcne$^{\cdot -}$ anions are involved in an extended face-to-face arrangement along rows of alternating 'donor' cations and 'acceptor' anions;[4] as noted this compound exhibits bulk ferromagnetic behaviour at temperatures below 4.8 K. Fig. 6 shows the magnetisation data for **2** recorded from 5.0 to 310 K and plotted as the inverse molar susceptibility (χ_m^{-1}) against temperature. The dependence of the observed molar susceptibility χ_m on temperature can be fitted to the sum of a Curie–Weiss term $\chi_{cw} = C(T - \theta)^{-1}$ and a diamagnetic term χ_d, *i.e.* $\chi_m = C(T - \theta)^{-1} + \chi_d$ such that a plot of χ_m^{-1} *versus* temperature affords a straight line. The Curie–Weiss constant, θ, derived from the linearised plot of χ_m^{-1} *versus* T, equals +0.08 K. This value is substantially smaller than that typically associated with ferromagnetic coupling, *e.g.* θ = +30 K for

$[Fe(\eta\text{-}C_5Me_5)_2][tcne]$,[4] and is indicative of very weak, if any, magnetic interactions between the spins on the $[Fe_2(\eta\text{-}C_5Me_5)_2\text{-}(\mu\text{-}SEt)_2(CO)_2]^{\cdot+}$ and tcne$^{\cdot-}$ radical ions. For the reasons discussed above the lack of significant magnetic interactions is not unexpected. In accord with the lack of magnetic interactions the effective magnetic moment [$\mu_{eff} = (8\chi T)^{\frac{1}{2}}$] for **2** is essentially constant over the temperature range ≈ 50 to 310 K. The average value of 3.46 μ_B is somewhat larger than that of 2.45 μ_B predicted for two independent non-interacting spins, possibly as a result of orbital angular-momentum contributions to the magnetic moment.

Conclusion

The two electron-transfer salts described in this paper have in common the dinuclear organometallic radical cation $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]^{\cdot+}$, the only difference being the nature of the planar polycyanohydrocarbon acceptor anion. The tcnq salt exhibits a structural motif in the solid state which is different from that found for the tcne salt, thus providing an illustration of the effect of anion size on crystal structure. The $\cdots D^{\cdot+}(A)_2{}^{2-}D^{\cdot+}D^{\cdot+}(A)_2{}^{2-}D^{\cdot+}D^{\cdot+}\cdots$ motif observed for the tcnq salt is not compatible with extended magnetic interactions in the crystal because of the wide separation of the unpaired spins on the donor cations by the diamagnetic $(tcnq)_2{}^{2-}$ dimers. The structural motif of alternating donor cations and acceptor anions observed for the tcne salt is one normally associated with co-operative magnetic behaviour. However, close examination of the crystal packing shows that there are two crystallographically independent tcne$^{\cdot-}$ anions in the $\cdots D^{\cdot+}A_A{}^{\cdot-}D^{\cdot+}A_B{}^{\cdot-}D^{\cdot+}A_A{}^{\cdot-}D^{\cdot+}A_B{}^{\cdot-}\cdots$ sequence (labelled A and B), which define different angles to the planes of the adjacent C_5Me_5 rings of 4 and 72°. This contrasts the situation found in $[Fe(\eta\text{-}C_5Me_5)_2][tcne]$[4] ($\theta = 16.8$ K) where the planes of the C_5Me_5 rings and tcne$^{\cdot-}$ anions are arranged face to face in an extended linear array of alternating cations and anions. Extended magnetic interactions in $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2][tcne]$ are therefore unlikely, as confirmed by the results of the variable-temperature magnetic measurements. Nevertheless, by suitable choice of acceptor anion it is possible to obtain an electron-transfer salt of $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2]^{\cdot+}$ which exhibits face-to-face stacking of alternating cations and anions of the type found in $[Fe(\eta\text{-}C_5Me_5)_2][tcne]$; the $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SEt)_2(CO)_2][dmdcnqi]$ compound is an example.[8] However, as previously noted, this salt does not exhibit co-operative magnetic interactions either, probably because of the low spin density associated with the large dinuclear cation.

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