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Synthesis and magnetic studies of the metallocarborane sandwich salts $[Fe(C_5Me_5)_2][M(C_2B_9H_{12})_2)]$ (M = Cr, Fe, Ni)

Jennifer M. Forward [a], D. Michael P. Mingos [b] and Anthony V. Powell [c]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR (UK)*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY (UK)*
[c] *Department of Chemistry, Heriott-Watt University, Edinburgh (UK)*

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Abstract

The salts $[Fe(C_5Me_5)_2][M(C_2B_9H_{11})_2)]$, (M = Cr, Fe, Ni), have been prepared by metathesis of $[Fe(C_5Me_5)_2]Cl$ and $[(CH_3)_4N][M(C_2B_9H_{11})_2)]$, (M = Cr, Fe, Ni), and the three salts have been shown to be isostructural from powder X-ray diffraction studies. The structure of the salt $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2)]$ has been determined by a single crystal X-ray diffraction study. The anions and cations pack in a distorted CsCl-type structure in which the distortion is thought to arise from the non-spherical shape of the $[Fe(C_2B_9H_{11})_2)]^-$ anion. The solid-state magnetic susceptibility data for all three salts can be fitted to the Curie–Weiss law between 6 and 296 K. Low values of θ indicate there are no significant ferromagnetic or antiferromagnetic interactions between the unpaired spins, even at low temperatures.

Key words: Ferrocene; Metallocarborane; Ferromagnetism; Charge transfer; X-ray diffraction; Crystal structure

1. Introduction

The synthesis and characterisation of molecular materials that show interesting magnetic properties are currently the subject of intensive investigation. The discovery by Miller of a charge-transfer salt, $[Fe(C_5Me_5)_2][TNCE]$, which exhibits bulk ferromagnetic coupling with a Curie temperature (T_C) of 4.8 K has led to the synthesis of a range of compounds that have the potential to show magnetic ordering [1–6]. The development of such molecular-based materials that show ferromagnetism with high Curie temperatures may prove to be technologically important; in, for example, the development of magnetic materials based on plastics. The research has so far focussed on organometallic charge-transfer salts that contain organometallic cations and planar organic anions and the magnetic properties of only a few charge-transfer salts that contain inorganic anions have been investigated [7]. In this paper we report the synthesis of a range of novel salts in which the cation is the decamethylmetallocenium ion, $[Fe(C_5Me_5)_2]^+$, and the anion is a metallocarborane sandwich complex of the general formula $[M(C_2B_9H_{11})_2]^-$, (M = Cr, Fe, Ni). Although many aspects of the chemistries of metallocarboranes have been studied previously their potential as components in the molecular design of magnetic materials has not previously been addressed. The magnetic properties of these salts were investigated over a range of temperatures, 6–297 K, and a range of magnetic field strengths, 0–4 tesla, by use of a SQUID magnetometer.

2. Results and Discussion

2.1. *Synthesis and characterisation of $[Fe(C_5Me_5)_2]$-$[M(C_2B_9H_{11})_2)]$, 1 (M = Fe, 1a; Ni, 1b; Cr, 1c)*

The decamethylferrocenium cation, $[Fe(C_5Me_5)_2]^+$, was prepared as the chloride salt by the oxidation of $[Fe(C_5Me_5)_2]$ with chlorine gas. A solution of this salt in methanol was added to a solution of $(CH_3)_4N[M(C_2B_9H_{11})_2]$, also in methanol, causing the precipitation of the product, $[Fe(C_5Me_5)_2][M(C_2B_9H_{11})_2)]$, **1**. Single crystals of **1** were grown from a solvent mixture of acetone/water. All three of the salts, **1a**, **1b** and **1c**,

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Correspondence to: Professor D.M.P. Mingos.

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were characterised by elemental microanalysis, infrared spectroscopy, FAB mass spectrometry, and magnetic susceptibility measurements. The structure of $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2)]$, **1a**, was determined by a single crystal X-ray study and is described below. The salts **1b** and **1c** were shown to be isostructural with **1a** from the powder X-ray diffraction patterns, which showed a similar number of peaks with similar relative intensities. In addition, the atomic positions for the salt $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2)]$, as determined by single crystal X-ray diffraction data, were used as input to the LAZY PULVERIX computer program [8], thereby enabling calculation of a simulated powder X-ray diffraction pattern. Comparison of the calculated 2θ values and relative intensities with measured data for each of the three salts permitted assignment of the *hkl* values to each of the observed reflections. This confirmed that the samples were, within the limits of experimental data, single phase materials and isomorphous.

2.2. X-Ray structure determination of 1a

The salt **1a** crystallises in the monoclinic space group $P2_1/n$ (no. 14). The molecular structure together with the labelling scheme is shown in Fig. 1, selected bond lengths and angles are given in Table 1, and the positional parameters are given in Table 2.

The two $[C_2B_9H_{11}]^{2-}$ ligands are coordinated to the iron atom, Fe(3), through a five-membered bonding face, C_2B_3, forming a twelve-vertex carborane unit. The two C_2B_3 bonding faces are planar with a deviation from planarity of only ±0.01 Å and lie parallel to one another. The Fe(3) atom is positioned in between the two $[(C_2B_9H_{11}]$ units where the two distances from Fe(3) to the least-squares best C_2B_3 planes are 1.530 and 1.533 Å. The two carborane ligands are twisted with respect to each other by approximately 108°. The bond lengths within the cages are in the ranges expected; C–C = 1.636(9), 1.640(9), C–B = 1.67(1)–1.76(1) and B–B = 1.75(1)–1.81(1). In the cation $[Fe(C_5Me_5)_2]^+$ the two C_5 rings are both planar, with deviations from planarity of only ±0.01 Å, and lie parallel to one another in an eclipsed conformation. The methyl groups lie slightly out of the plane of the ring away from the central iron atom at a distance of 0.06–0.11 Å. The Fe(1) atom is positioned in between the two $[(C_5Me_5)]$ rings and the two distances from Fe(1) to the least-squares best C_5 planes are 1.720 and 1.718 Å.

The most interesting aspect of the crystal structure of $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2)]$ is the three-dimensional arrangements of the anions and cations within the lattice. A study by Mingos and Rohl on the packing of soft salts has suggested that the relative sizes of the ions is the primary factor in determining their solid state structure [9]. The distortions away from the idealised structures of simple ionic salts arise from the deviations of the ions from the ideal spherical shape. The computer program VOLUME written by Rohl was used to calculate the molecular volume, (V_m), of both the anion and cation in **1a**. By assuming that the

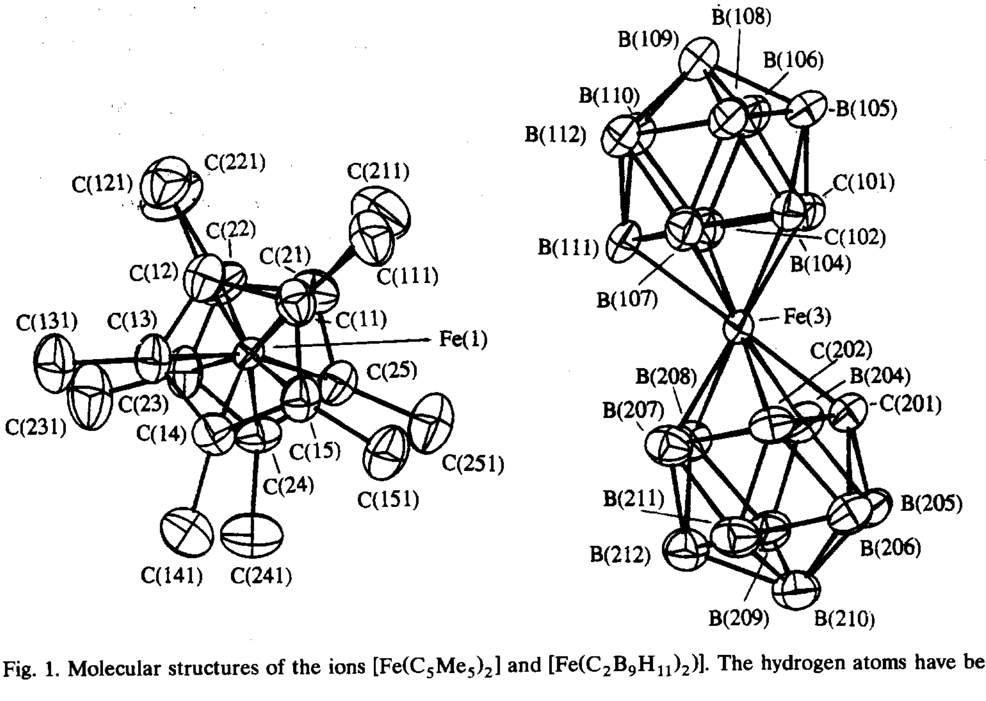

Fig. 1. Molecular structures of the ions $[Fe(C_5Me_5)_2]$ and $[Fe(C_2B_9H_{11})_2)]$. The hydrogen atoms have been omitted for reasons of clarity.

TABLE 1. Selected bond lengths (Å) and angles (°) for $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2)]$

Fe(1)–C(11)	2.091(7)	Fe(1)–C(21)	2.098(7)
Fe(1)–C(12)	2.079(7)	Fe(1)–C(22)	2.103(7)
Fe(1)–C(13)	2.085(7)	Fe(1)–C(23)	2.105(6)
Fe(1)–C(14)	2.100(6)	Fe(1)–C(24)	2.086(6)
Fe(1)–C(15)	2.102(7)	Fe(1)–C(25)	2.116(6)
C(11)–C(12)	1.394(9)	C(21)–C(22)	1.424(9)
C(11)–C(15)	1.388(9)	C(21)–C(25)	1.425(9)
C(12)–C(13)	1.424(9)	C(22)–C(23)	1.425(9)
C(13)–C(14)	1.419(9)	C(23)–C(24)	1.425(9)
C(14)–C(15)	1.414(9)	C(24)–C(25)	1.417(9)
C(11)–C(111)	1.52(1)	C(21)–C(211)	1.50(1)
C(12)–C(121)	1.500(9)	C(22)–C(221)	1.50(1)
C(13)–C(131)	1.49(1)	C(23)–C(231)	1.493(9)
C(14)–C(141)	1.496(9)	C(24)–C(241)	1.52(1)
C(15)–C(151)	1.518(9)	C(25)–C(251)	1.515(9)
Fe(3)–C(101)	2.091(6)	Fe(3)–C(201)	2.088(6)
Fe(3)–C(102)	2.090(6)	Fe(3)–C(202)	2.090(6)
Fe(3)–B(104)	2.125(7)	Fe(3)–B(204)	2.134(8)
Fe(3)–B(107)	2.106(8)	Fe(3)–B(207)	2.134(7)
Fe(3)–B(108)	2.148(8)	Fe(3)–B(208)	2.160(8)
C(101)–C(102)	1.636(9)	C(201)–C(202)	1.640(9)
C(101)–B(104)	1.71(1)	C(201)–B(204)	1.72(1)
C(101)–B(105)	1.73(1)	C(201)–B(205)	1.739(9)
C(101)–B(106)	1.76(1)	C(201)–B(206)	1.71(1)
C(102)–B(107)	1.67(1)	C(202)–B(207)	1.68(1)
C(102)–B(106)	1.71(1)	C(202)–B(206)	1.71(1)
C(102)–B(111)	1.69(1)	C(202)–B(211)	1.72(1)
C(102)–B(111)	1.69(1)	C(202)–B(211)	1.72(1)
B(104)–B(105)	1.80(1)	B(204)–B(205)	1.81(1)
B(104)–B(108)	1.79(1)	B(204)–B(208)	1.81(1)
B(104)–B(109)	1.80(1)	B(204)–B(209)	1.82(1)
B(105)–B(106)	1.78(1)	B(205)–B(206)	1.77(1)
B(105)–B(109)	1.78(1)	B(205)–B(209)	1.79(1)
B(105)–B(110)	1.78(1)	B(205)–B(210)	1.75(1)
B(106)–B(110)	1.77(1)	B(206)–B(210)	1.77(1)
B(106)–B(111)	1.75(1)	B(206)–B(211)	1.78(1)
B(107)–B(108)	1.77(1)	B(207)–B(208)	1.77(1)
B(107)–B(111)	1.75(1)	B(207)–B(211)	1.78(1)
B(107)–B(112)	1.76(1)	B(207)–B(212)	1.75(1)
B(108)–B(109)	1.80(1)	B(208)–B(209)	1.80(1)
B(108)–B(112)	1.81(1)	B(208)–B(212)	1.80(1)
B(109)–B(110)	1.79(1)	B(209)–B(210)	1.79(1)
B(109)–B(112)	1.79(1)	B(209)–B(212)	1.76(1)
B(110)–B(111)	1.77(1)	B(210)–B(211)	1.79(1)
B(110)–B(112)	1.77(1)	B(210)–B(212)	1.80(1)
B(111)–B(112)	1.78(1)	B(211)–B(212)	1.77(1)
C(11)–C(12)–C(13)	108.2(6)	C(21)–C(22)–C(23)	108.0(6)
C(12)–C(13)–C(14)	106.8(6)	C(22)–C(23)–C(24)	107.9(6)
C(13)–C(14)–C(15)	107.8(6)	C(23)–C(24)–C(25)	108.0(6)
C(14)–C(15)–C(11)	108.2(6)	C(24)–C(25)–C(21)	108.3(6)
C(15)–C(11)–C(12)	109.0(7)	C(25)–C(21)–C(22)	107.7(6)
C(111)–C(11)–C(12)	125.9(7)	C(211)–C(21)–C(22)	126.0(7)
C(121)–C(12)–C(13)	126.7(7)	C(221)–C(22)–C(23)	125.6(6)
C(131)–C(13)–C(14)	126.5(7)	C(231)–C(23)–C(24)	125.1(6)
C(141)–C(14)–C(15)	126.8(6)	C(141)–C(14)–C(15)	126.1(6)
C(151)–C(15)–C(11)	127.2(7)	C(151)–C(15)–C(11)	124.5(67)
B(104)–C(101)–C(102)	110.0(5)	B(204)–C(201)–C(202)	110.8(5)
C(101)–C(102)–B(107)	111.1(5)	C(201)–C(202)–B(207)	111.4(5)
C(102)–B(107)–B(108)	107.7(5)	C(202)–B(207)–B(208)	106.8(5)

TABLE 1 (continued)

B(107)–B(108)–B(104)	105.0(6)	B(207)–B(208)–B(204)	106.2(5)
B(108)–B(104)–C(101)	106.1(5)	B(208)–B(204)–C(201)	104.7(5)
B(105)–B(106)–B(111)	108.0(6)	B(205)–B(206)–B(211)	107.1(6)
B(106)–B(111)–B(112)	108.8(6)	B(206)–B(211)–B(212)	107.4(6)
B(111)–B(112)–B(109)	107.4(6)	B(211)–B(212)–B(209)	109.2(6)
B(112)–B(109)–B(105)	107.5(6)	B(212)–B(209)–B(205)	107.2(6)
B(109)–B(105)–B(106)	108.4(6)	B(209)–B(205)–B(206)	109.0(6)
B(106)–C(101)–B(105)	61.3(4)	B(206)–C(201)–B(205)	61.8(4)
B(111)–C(102)–B(106)	62.2(4)	B(211)–C(202)–B(206)	63.1(4)
B(111)–B(107)–B(112)	61.0(5)	B(211)–B(207)–B(212)	60.2(5)
B(112)–B(108)–B(109)	59.5(4)	B(212)–B(208)–B(209)	58.7(5)
B(105)–B(104)–B(109)	59.1(5)	B(205)–B(204)–B(209)	58.6(4)

molecular ions are spherical, an effective radius, R_{eff}, based on the molecular volume was calculated from the following equation:

$$R_{\mathrm{eff}}(V_{\mathrm{m}}) = \sqrt[3]{\frac{3V_{\mathrm{m}}}{4\pi}}$$

In addition, the VOLUME program was used to describe the molecular shapes of the anion and cation. The moments of inertia M_1, M_2 and M_3 were calculated from the summation of the x, y and z cartesian coordinates of each atom in the ion where M_1 is the largest moment and M_3 is the smallest moment. From these three moments three indices, F_{s}, F_{c} and F_{d}, have been defined that can be used to describe the molecular shapes of the ions. The closer an index is to unity, the closer the molecule is to the geometry represented by the index.

$$F_{\mathrm{s}} = \frac{M_3}{M_1} \quad \text{Spherical Index}$$

$$F_{\mathrm{c}} = 1 - \frac{M_2 + M_3}{2M_1} \quad \text{Cylindrical Index}$$

$$F_{\mathrm{d}} = 1 - \frac{2M_3}{M_1 + M_2} \quad \text{Discoidal Index}$$

Table 3 summarises the information generated by the VOLUME program for the anion $[\mathrm{Fe(C_2B_9H_{11})_2}]^-$ and the cation $[\mathrm{Fe(C_5Me_5)_2}]^+$ on the molecular size and shape of the two ions.

The results in Table 3 for $[\mathrm{Fe(C_2B_9H_{11})_2}]^-$ imply that the anion has a cylindrical shape, with one of the moments is large and the other two small. The closest index to unity is F_{c}, the cylindrical index. In contrast, the $[\mathrm{Fe(C_5M_5)_2}]^+$ cation is very close to spherical in shape, with the three moments of inertia almost equal, and the closest index to unity is F_{s}, the spherical index. The volumes and R_{eff} of the two ions are approximately the same, giving a calculated anion/cation radius (a/c) of 0.98. Rohl found in his study [9] that eight-coordinate CsCl and antifluorite structures were observed when a/c lay between 0.99 and 0.93 and the results found for $[\mathrm{Fe(C_5Me_5)_2}][\mathrm{Fe(C_2B_9H_{11})_2}]$ agree with these findings. The packing found for the soft salt $[\mathrm{Fe(C_5Me_5)_2}][\mathrm{Fe(C_2B_9H_{11})_2}]$ is based on the eight-coordinate CsCl structure, as shown in Fig. 2, where both the anion and cation have been assumed to be spherical. However, Fig. 2 shows that the packing is distorted from the idealised CsCl structure, and it is thought that this distortion arises from the cylindrical shape of the $[\mathrm{Fe(C_2B_9H_{11})_2}]^-$ anion. Figure 3 shows the coordination of the eight cations around a central anion with the ions represented as ellipsoids generated from the VOLUME program. This figure illustrates the distortion from the ideal CsCl packing of the eight cations in which the four cations around the centre of the anion approach closer than the four at the two ends of the anion. This can also be seen in Table 4, which shows the distances between the centroid of the anion and its eight nearest neighbour cations. The anion-cation distances vary from 6.97–9.96 Å, with four shorter distances to the central anion and four longer distances. Figure 4 shows the coordination of the eight anions around the central cation. The figure demonstrates the way in which the anions pack in a herring-bone pattern in order to minimise the steric repulsions between the anions.

Also shown in Table 4, are the anion–anion distances and the cation–cation distances. The first six cation–cation distances are very similar, varying from 8.98–9.63 Å, after which the next closest is 12.13 Å. This is expected if comparison is made with an idealised CsCl structure in which there are six cations around a central cation at approximately equal distances. In contrast, the anion–anion distances show no pattern where the first six vary from 8.40–11.05 Å, and the next distance is 11.36 Å. This is another feature of the packing that arises from the non-spherical shape of the anions.

TABLE 2. Fractional coordinates and isotropic temperature factors (Å^2) for $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2]$

Atom	x	y	z	U_{iso}
Fe(1)	0.62886(5)	0.17632(7)	0.30333(8)	0.0268
Fe(3)	0.35502(5)	−0.22376(7)	0.19050(7)	0.0280
C(11)	0.6123(4)	0.0950(5)	0.1730(5)	0.0454
C(12)	0.6709(4)	0.1621(6)	0.1875(5)	0.0426
C(13)	0.6393(4)	0.2559(5)	0.1846(5)	0.0398
C(14)	0.5602(4)	0.2435(5)	0.1674(5)	0.0395
C(15)	0.5446(4)	0.1435(5)	0.1609(5)	0.0408
C(21)	0.6476(4)	0.0867(5)	0.4292(5)	0.0423
C(22)	0.7152(4)	0.1412(6)	0.4434(5)	0.0427
C(23)	0.6963(4)	0.2407(5)	0.4421(5)	0.0413
C(24)	0.6166(4)	0.2476(5)	0.4258(5)	0.0386
C(25)	0.5874(4)	0.1529(5)	0.4213(5)	0.0382
C(111)	0.6194(5)	−0.0132(6)	0.1643(6)	0.0725
C(121)	0.7511(4)	0.1382(7)	0.1958(6)	0.0686
C(131)	0.6797(4)	0.3492(6)	0.1881(6)	0.0661
C(141)	0.5032(4)	0.3232(6)	0.1526(6)	0.0649
C(151)	0.4657(4)	0.0997(6)	0.1382(6)	0.0652
C(211)	0.6426(4)	−0.0208(5)	0.4325(6)	0.0584
C(221)	0.7939(4)	0.1013(6)	0.4619(6)	0.0604
C(231)	0.7520(4)	0.3219(6)	0.4588(6)	0.0604
C(241)	0.5740(4)	0.3400(6)	0.4276(6)	0.0642
C(251)	0.5064(4)	0.1241(6)	0.4090(6)	0.0576
C(101)	0.4572(3)	−0.2637(5)	0.3076(5)	0.0443
C(102)	0.4020(3)	−0.3556(5)	0.2552(5)	0.0373
C(201)	0.2491(3)	−0.1944(5)	0.0755(5)	0.0426
C(202)	0.2408(3)	−0.2493(5)	0.1731(5)	0.0380
B(104)	0.4724(4)	−0.1954(6)	0.2163(6)	0.0417
B(105)	0.5445(4)	−0.2781(6)	0.2935(6)	0.0443
B(106)	0.4973(4)	−0.3798(6)	0.3199(7)	0.0450
B(107)	0.3762(4)	−0.3541(6)	0.1296(6)	0.0363
B(108)	0.4208(4)	−0.2535(6)	0.0980(6)	0.0462
B(109)	0.5226(4)	−0.2735(6)	0.1607(7)	0.0491
B(110)	0.5366(4)	−0.3870(6)	0.2242(7)	0.0488
B(111)	0.4447(4)	−0.4363(6)	0.2044(6)	0.0418
B(112)	0.4607(4)	−0.3732(7)	0.1047(6)	0.0442
B(204)	0.3062(4)	−0.0936(6)	0.1134(6)	0.0397
B(205)	0.2025(4)	−0.0861(6)	0.0577(6)	0.0430
B(206)	0.1619(4)	−0.1891(6)	0.0922(6)	0.0401
B(207)	0.2898(4)	−0.1913(6)	0.2819(6)	0.0394
B(208)	0.3320(5)	−0.0887(6)	0.2493(6)	0.0452
B(209)	0.2524(5)	−0.0176(6)	0.1684(7)	0.0491
B(210)	0.1639(5)	−0.0769(6)	0.1525(7)	0.0498
B(211)	0.1876(4)	−0.1844(6)	0.2276(6)	0.0450
B(212)	0.2440(5)	−0.0797(7)	0.2721(6)	0.0469

Figure 5 shows a more extended picture of the packing in the salt. The $[Fe(C_2B_9H_{11})_2)]^-$ anions pack in a double herring-bone pattern, as illustrated schematically below in Fig. 6.

2.2.1. *Magnetic susceptibility*

The molar magnetic susceptibilities of the three salts, **1a**, **1b** and **1c**, were measured over the temperature range 6–296 K at two different magnetic fields, using a SQUID magnetometer. In the salt **1a** both the anion and cation have one unpaired electron and the ground state electronic configuration of both of the

TABLE 3. Molecular sizes and shapes of the constituent ions in $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2)]$

	Anion $[Fe(C_2B_9H_{11})_2)]^-$	Cation $[Fe(C_5Me_5)_2]^+$
Molecular volume		
(V_m) (Å^3)	286.5	303.8
R_{eff}(Å)	4.09	4.17
M_1	336	192
M_2	90	190
M_3	87	174
F_s	0.26	0.91
F_c	0.74	0.05
F_d	0.59	0.09

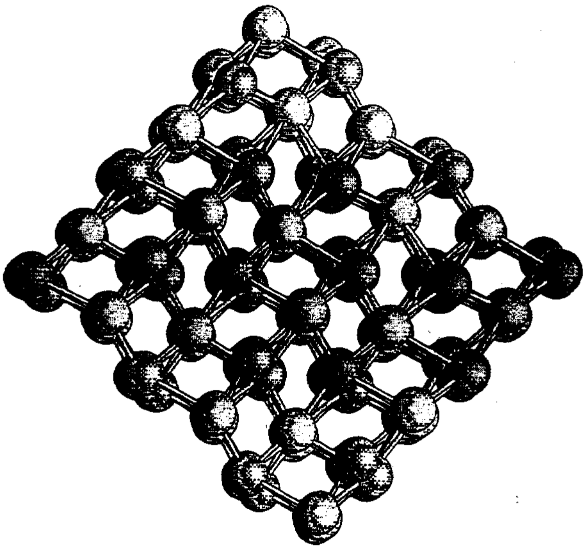

Fig. 2. A schematic illustration of the packing in $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2)]$.

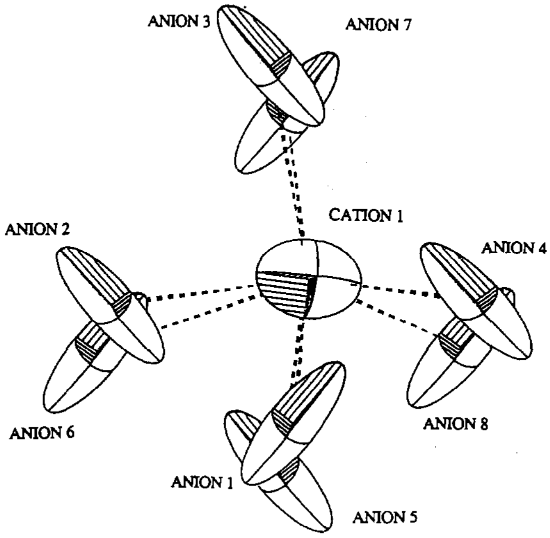

Fig. 3. Packing arrangement of the eight $[Fe(C_2B_9H_{11})_2)]^-$ anions around the central $[Fe(C_5Me_5)_2]^+$ cation.

TABLE 4. Inter-ion distances in $[\mathrm{Fe(C_5Me_5)_2}][\mathrm{Fe(C_2B_9H_{11})_2)}]$

Anion–cation (Å)	Anion–anion (Å)	Cation–cation (Å)
6.972	8.398	8.983
7.328	8.398	8.983
7.330	9.438	9.613
8.357	9.438	9.623
8.935	10.596	9.623
9.428	11.053	9.627
9.457	11.355	12.131
9.958		
12.790		

ions is $(a_{1g})^2(e_{2g})^3$. Over the temperature range measured the magnetic behaviour of the salt followed the Curie–Weiss law $[\chi_m = C/(T-\theta)]$ with $C = 1.71$ and $\theta = -5.8$ K, yielding an effective magnetic moment per magnetic ion of 2.61 μ_B. It was concluded that there are no significant ferromagnetic or antiferromagnetic interactions between the unpaired spins even at low temperatures and no transition to bulk ferromagnetic coupling. The experimental average moment per magnetic ion of 2.61 μ_B is high compared to the spin-only value for two non-interacting $S = \frac{1}{2}$ species (1.73 μ_B), suggesting that there are orbital contributions to the moment over and above the spin only value. These orbital contributions to the moment have been observed in other ferrocenium salts and iron(III) metallocarborane complexes [10].

The salt **1b** contains the anion $[\mathrm{Ni(C_2B_9H_{11})_2}]^-$, in which the $\mathrm{Ni^{III}}$ has the ground-state electronic configuration $(a_{1g})^2(e_{2g})^4(e_{1g})^1$. It also showed magnetic behaviour that indicated that the two $S = \frac{1}{2}$ spins do not interact even at low temperatures. The salt obeyed the Curie–Weiss law over the temperature range studied, with $C = 1.94$ and $\theta = 3.7$ K, yielding an effective moment per magnetic ion of 2.8 μ_B. As with the salt **1a** this value of the calculated effective moment is higher than the calculated spin-only value of 1.73 μ_B, implying significant orbital contribution to the magnetic moment.

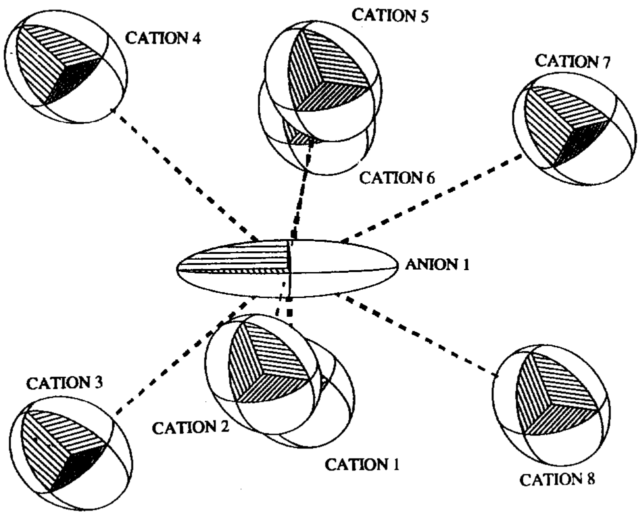

Fig. 4. Packing of the eight $[\mathrm{Fe(C_5Me_5)_2}]^+$ cations around the central $[\mathrm{Fe(C_2B_9H_{11})_2)}]^-$ anion.

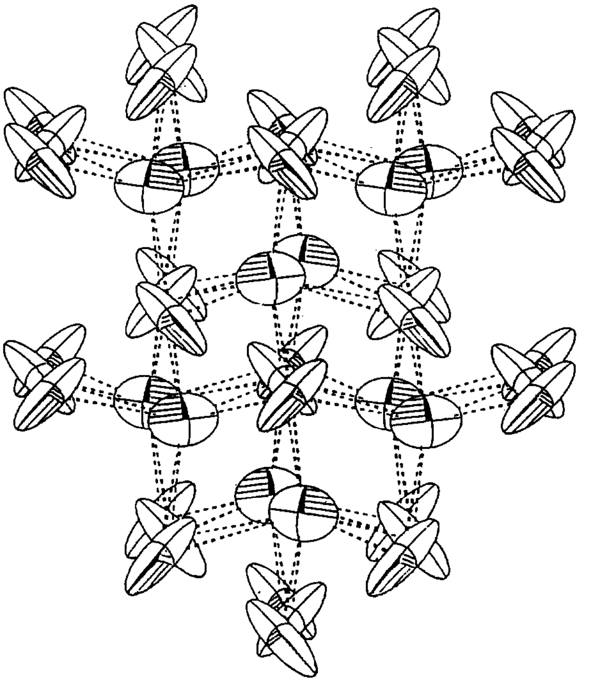

Fig. 5. Extended packing diagram of $[\mathrm{Fe(C_5Me_5)_2}][\mathrm{Fe(C_2B_9H_{11})_2)}]$ with both ions represented by their respective elipsoids.

The salt **1c**, containing $\mathrm{Cr^{III}}$ with a ground-state configuration of $(a_{1g})^1(e_{2g})^2$, also obeyed the Curie–Weiss law, with $C = 2.7$ and $\theta = 3.0$ K, yielding an effective moment per magnetic ion of 3.3 μ_B, a value closer to the calculated spin-only value of 3.0 μ_B. Again, this implies that the system is magnetically dilute and that there are no significant ferromagnetic

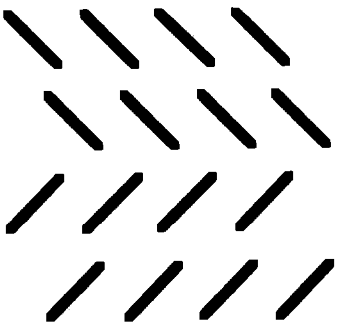

Fig. 6. Schematic representation of the double herring-bone packing of the $[\mathrm{Fe(C_2B_9H_{11})_2)}]^-$ anions.

or antiferromagnetic interactions between the unpaired spins. In all three salts the molar susceptibility was independent of the field strength, providing further evidence for the absence of cooperative magnetic behaviour.

3. Conclusions

It appears from the results obtained from this study that one of the conditions necessary for the observation of bulk ferromagnetism in a charge-transfer salt based on sandwich compounds is the presence of one-dimensional linear chains of either anions or cations. Clearly the salts $[Fe(C_5Me_5)_2][M(C_2B_9H_{11})_2)]$, **1**, do not form chains of this sort, packing instead in a distorted three dimensional packing mode based on the CsCl-type structure. In addition, it appears that the electron delocalisation in metallocarboranes is primarily localised on the metal bonding face and not throughout the cage [11], thereby limiting the extent of inter-ion interactions. The distance between the unpaired spins of the anion and cation is too large for the cooperative magnetic exchange to be significant. The packing of the molecular salt $[Fe(C_5Me_5)_2][M(C_2B_9H_{11})_2)]$ has been satisfactorily analysed by use of the method developed in ref. 9.

4. Experimental details

4.1. General

All preparations and reactions were carried out under nitrogen by use of standard Schlenk-tube and vacuum-line techniques. Solvents were pre-dried by standing over activated molecular sieves and subsequently refluxed over a suitable drying agent under nitrogen.

4.2. Equipment

Infra-red spectra were recorded on a Perkin-Elmer FT-1710 spectrometer as Nujol mulls between KBr discs. The FAB mass spectra were recorded on a VG ZAB-E high resolution double-focussing mass spectrometer at the University of Swansea.

The magnetic susceptibility data was collected over the temperature range 6–296 K by using a Cryogenic Consultants SCU 500 Superconducting Quantum Interference Device (SQUID) susceptometer. The susceptibilities were corrected for the intrinsic diamagnetism of the sample container and the diamagnetism of the electronic cores of the constituent atoms, estimated from Pascal's constants [12]. Crystallographic calculations were performed on a Micro Vax 3000 computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system [13]. The powder X-ray data were recorded on a Philips vertical diffractometer.

Elemental microanalyses were performed in the analytical services department of the Inorganic Chemistry Laboratory, Oxford.

4.3. Syntheses

The decamethylferrocenium cation $[Fe(C_5Me_5)_2]^+$ was formed by oxidation of $[Fe(C_5Me_5)_2]$. Chlorine gas was bubbled through a toluene solution of $[Fe(C_5Me_5)_2]$, causing the precipitation of a green solid. This solid was isolated and recrystallised from dichloromethane/toluene to give green crystals of $[Fe(C_5Me_5)_2]Cl$. The three salts $[(CH_3)_4N][Fe(C_2B_9H_{11})_2]$, (M = Cr, Fe, Ni), were synthesised by procedures developed by Hawthorne and co-workers [14,15].

4.3.1. *$[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2)]$, 1a*

$[(CH_3)_4N][Fe(C_2B_9H_{11})_2]$ (0.0345 g, 0.087 mmol) was dissolved in methanol (15 cm^3) and a solution of $[Fe(C_5Me_5)_2]Cl$ (0.0313 g, 0.087 mmol) in methanol (10 cm^3) was added. The mixture was stirred for 30 min, during which a brown precipitate was formed. This precipitate was recrystallized from acetone-water to give red/brown crystals of $[Fe(C_5Me_5)_2][Fe(C_2B_9H_{11})_2]$ (yield = 85%). Anal. Calcd for $C_{24}H_{52}B_{18}Fe_2$: C, 44.5; H, 8.0. Found: C, 44.4; H, 8.0. I.R. data: ν(B–H) 2568s, 2569s, 2539s cm^{-1}; ν(methyl C–H) 1376m, 1475w cm^{-1}. Positive ion FAB-MS: $[M]^+ = 326$. Negative ion FAB-MS: $[M]^- = 320$.

4.3.2. *$[Fe(C_5Me_5)_2][Ni(C_2B_9H_{11})_2]$, 1b*

$[(CH_3)_4N][Ni(C_2B_9H_{11})_2]$ (0.042 g, 0.105 mmol) was dissolved in methanol (20 cm^3) and a solution of excess $[Fe(C_5Me_5)_2]Cl$ (0.038 g, 0.105 mmol) was added. The mixture was stirred for 30 min during which a green precipitate was formed. This precipitate was recrystallised from acetone-water to give 0.05 g of dark green crystals (yield = 78%) of $[Fe(C_5Me_5)_2][Ni(C_2B_9H_{11})_2]$. Anal. Calcd for $C_{24}H_{52}B_{18}FeNi$: C, 44.5; H, 8.0. Found: C, 44.5; H, 7.9. I.R. data: ν(B–H) 2063s cm^{-1}; ν(methyl C–H) 1376m, 1476w cm^{-1}. Positive ion FAB-MS: $[M]^+ = 326$. Negative ion FAB-MS: $[M]^- = 323$.

4.3.3. *$[Fe(C_5Me_5)_2][Cr(C_2B_9H_{11})_2]$, 1c*

$[(CH_3)_4N][Cr(C_2B_9H_{11})_2]$ (0.7 g, 1.8 mmol) was dissolved in methanol (20 cm^3) and a solution of $[Fe(C_5Me_5)_2]Cl$ (0.7 g, 1.9 mmol) in methanol (15 cm^3) was added. The mixture was stirred for 30 min during which a dark red precipitate was formed. This was recrystallized from acetone-water to give dark-red crystals of $[Fe(C_5Me_5)_2][Cr(C_2B_9H_{11})_2]$ (yield = 84%). Anal. Calcd for $C_{24}H_{52}B_{18}CrFe$: C, 45.3; H, 8.4. Found: C, 45.6; H, 8.7.

4.4. Crystal structure determination

Crystals of **1a** were sealed in Lindemann glass capillaries.

4.4.1. Crystal data

$C_{24}H_{52}B_{18}Fe_2$, $M = 591.1$, monoclinic space group $P2_1/n$ (no. 14), $a = 18.716(2)$, $b = 13.884(1)$, $c = 14.201(1)$ Å, $\beta = 111.76(8)°$, $U = 3427.1$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 1.5401$ Å). $Z = 4$, $D_c = 1.146$ g cm^{-3}, $F(000) = 1248$. Dark red air-stable tablets, dimensions $0.48 \times 0.20 \times 0.13$ mm^3.

4.4.2. Data collection and processing

CAD4 diffractometer, $\omega - 2\theta$ mode with ω scan width $= 0.70 + 0.15 \tan \theta$, Cu/K$\alpha$ radiation; 6267 reflections measured ($0 \leq \theta \leq 45$, $\pm h, k, l$), 2767 unique (merging $R = 0.037$ after absorption correction), giving 2199 with $I \geq 3\sigma(I)$.

4.4.3. Structure analysis and refinement

Direct methods (Fe atoms) followed by normal heavy atom procedures. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms on the carborane anion were located by difference Fourier syntheses and the hydrogen atoms on the cation were calculated in idealised positions. None of these hydrogen atoms were included in the final cycles of refinement. The vibrations between bonded atoms in the two carborane cages were restrained so that the mean square displacement along the bond direction of two atoms that form a bond is zero, with an e.s.d. of 0.01 Å^2. In addition, similarity restraints (with an e.s.d. of 0.02 Å^2) were applied to the temperature factors of pairs of bonded atoms. Each (C_5Me_5) ligand was treated in a similar way. All of the non-hydrogen atoms were then assigned anisotropic thermal parameters and the positional and anisotropic thermal parameters of these atoms were refined by full-matrix least-squares refinement. The application of the restraints did not significantly alter the bond lengths in either the cation or the anion. The results of the refinement were analysed in terms of the overall rigid-body motion tensors L, T and S. Developed by Schomaker and Trueblood [16], the rigid-body motion of molecules can be described in terms of three tensors, one for libration, one for translation and one for the correlation of libration and translation. The results indicated that the carborane anion $[Fe(C_2B_9H_{11})_2]^-$ acts as a rigid body having essentially isotropic molecular vibration and libration tensors. *TLS* analysis of the (C_5Me_5) ligands showed that each of the ligands was librating about an axis approximately perpendicular to the plane of the ligands with an amplitude of about 20° [2]. Using X-ray structure analysis it is not possible to determine the relationship between the librations of the two (C_5Me_5) groups. The correlations between the temperature factors of the atoms in each (C_5Me_5) group are evident in the thermal ellipsoid plot of the $[Fe(C_5Me_5)_2]$-$[Fe(C_2B_9H_{11})_2]$ salt. The results of the *TLS* analysis also indicated that the restraints of the vibrations used in the refinement were valid in that the carbon atoms move as part of a rigid group, not as individual atoms. The restraints used in the model augmented the X-ray observations by an additional 560 observations of restraint. When the restraints were removed and the structure re-refined the bond lengths in the molecule did not change significantly. A three-term Chebychev weighting scheme was applied with coefficients 13.3, −8.94, 9.80. Final R and R' values are 0.040, 0.045.

A complete list of bond lengths and angles and a table of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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