

The magnetic and second-order nonlinear optical properties of some paramagnetic salts containing metallocarborane anions

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Abstract

A series of air-stable salts containing the paramagnetic metallocarboranes $[\text{MCb}_2]^-$ ($\text{M} = \text{Fe}, \text{Ni}; \text{Cb}^{2-} = 7,8\text{-C}_2\text{B}_9\text{H}_{11}^{2-}$) has been prepared and their magnetic properties investigated. The paramagnetic salts $[\text{Fe}^{\text{III}}\text{Tp}_2][\text{Fe}^{\text{III}}\text{Cb}_2]$ ($\text{Tp} = \text{HB}(\text{C}_3\text{H}_3\text{N}_2)_3$), $[\text{Fe}^{\text{III}}\{\text{C}_6\text{H}_4(\text{O}(\text{C}(\text{Me})=\text{N}(\text{CH}_2)_2\text{NHCH}_2)_2\}][\text{Fe}^{\text{III}}\text{Cb}_2]$, $[\text{C}_5\text{H}_5\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$, $[4\text{-MeC}_5\text{H}_4\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$, $[4\text{-PhC}_5\text{H}_4\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$, $[\text{C}_9\text{H}_7\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$, $[\text{Fe}^{\text{III}}\text{Tp}_2][\text{TCNQ}]$ and $[\text{Fe}^{\text{III}}\text{Cp}_2][\text{Fe}^{\text{III}}\text{Cb}_2]$ have been isolated. Magnetic susceptibility measurements show that these salts exhibit typical paramagnetic behaviour with no evidence of cooperative magnetic interactions over the temperature range 6–300 K. The salts $[E\text{-Fc-CH}=\text{CH-}p\text{-C}_5\text{H}_4\text{NMe}][\text{M}^{\text{III}}\text{Cb}_2]$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Co}$) were also synthesised and their second-order nonlinear optical properties assessed using the Kurtz powder test. Only the cobalt-containing complex gave detectable, though weak, second harmonic generation of 0.01 times urea at 1.907 μm . The salt $[\text{C}_5\text{H}_5\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$ exhibits SHG with an efficiency of 0.5 times urea at 1.907 μm and 0.1 at 1.064 μm . Mass spectrometric and $^{13}\text{C}\{^1\text{H}\}$ NMR studies of the products formed by the degradation of $[\text{Co}(\text{Cb})_2]^-$ by base in the presence of Co^{2+} ions has provided no evidence for the formation of higher oligomers than the previously reported $\{[\text{Co}(\text{Cb})_2]_2(\text{C}_2\text{B}_8\text{H}_{10})\}^{2-}$ and $\{[\text{CoCb}(\text{C}_2\text{B}_8\text{H}_{10})_2\text{Co}]\}^{3-}$. The structures of $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{Ni}^{\text{III}}\text{Cb}_2]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and $[4\text{-MeC}_5\text{H}_4\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$ have been determined by single crystal X-ray diffraction studies. © 1997 Elsevier Science S.A.

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1. Introduction

The discovery by Miller et al. [1,2] that the salt $[\text{FeCp}_2^*][\text{TCNE}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{TCNE} = \text{tetracyanoethene}$) exhibits ferromagnetic interactions, and spontaneous magnetisation at low temperatures has stimulated renewed interest in the magnetic properties of organometallic compounds [3,4]. However, the mechanism of the magnetic cooperativity in $[\text{FeCp}_2^*][\text{TCNE}]$ is still controversial, and the application of the model proposed by McConnell [5,6] and Breslow et al. [7] to compounds of Miller and Epstein [8] has been questioned [9]. It is important, therefore, for synthetic

chemists to search for new examples of molecular ferri- or ferromagnets, against which theories of magnetic interaction can be tested. The metallocarborane anions $[\text{MCb}_2]^-$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Cu}; \text{Cb}^{2-} = \text{nido-7,8-C}_2\text{B}_9\text{H}_{11}^{2-}$) offer a highly appropriate starting point for such studies since they are related to metallocenes but, because the Cb^{2-} ligand can stabilise high metal oxidation states, they provide examples of air stable anions containing Fe(III), Ni(III) or Cu(III) [10,11]. The structure of the complexes $[\text{MCb}_2]^-$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Cu}$) precludes the ‘face-to-face’ interactions found in the structure of $[\text{FeCp}_2^*][\text{TCNE}]$. MeCN (although this is not the structure of the ferromagnetic material) [12]. However, the structure of the charge transfer compound formed between $[\text{NiCb}_2]$ and pyrene demonstrates that metallocarboranes can enter into intermolecular charge transfer

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interactions but with the planar molecule oriented in a direction perpendicular to that found in the metallocenes [13]. It is also known from EPR studies [14] of Co(II) metallocarboranes that the unpaired spin of the metal ion strongly influences atoms in the metal bonded $\{B_3C_2\}$ face. These observations suggested to us that salts containing $[MCb_2]^-$ ($M = Fe, Ni, Cu$) and paramagnetic cations would be of interest as a potential source of new ferromagnetic materials. Some salts containing planar diamagnetic ions were also prepared for comparison. Forward et al. [15,16] have independently prepared salts containing $[MCb_2]^-$ ($M = Cr, Fe, Ni$) and the cations TTF^+ or $[FeCp_2^*]^+$ and have reported the crystal structures of $[TTF][FeCb_2]$ and $[FeCp_2^*][FeCb_2]$. Here we describe the synthesis and magnetic properties of some additional salts of $[FeCb_2]^-$, which contain the paramagnetic cations $[E-Fc-CH=CH-p-C_5H_4NMe]^+$ [17], $[FeTp_2]^+$ ($Tp^- = \text{hydrotrispyrazol-1-ylborate}$) and $[Fe\{OC_6H_4-4-C(Me)=N(CH_2)_2NH(CH_2)_2\}]^+$ [18,19] or the diamagnetic cations *N*-methylpyridinium, *N*-methyl-4-phenylpyridinium and *N*-methylquinolinium. We also report the crystal structures of $[FeCp_2^*][NiCb_2]$ and $[MeNC_5H_4-4-Me][FeCb_2]$. Although the former was considered [16] to be isomorphous with $[FeCp_2^*][FeCb_2]$ on the basis of powder X-ray data, such data might not be sensitive to small structural differences such as the relative orientations of the Cb^{2-} ligands. The possible syntheses of higher oligomeric metallocarborane derivatives than the previously reported $[(CoCb(C_2B_8H_{10}))_2Co]^{3-}$ was also investigated.

2. Results and discussion

2.1. Synthetic studies

The salts $[Fe^{III}Tp_2][Fe^{III}Cb_2]$, $[Fe^{III}\{(OC_6H_4-4-C(Me)=N(CH_2)_2NH(CH_2)_2)\}_2][Fe^{III}Cb_2]$, $[C_5H_5NMe][Fe^{III}Cb_2]$, $[4-Ph-C_5H_9NMe][Fe^{III}Cb_2]$, $[C_9H_7NMe][Fe^{III}Cb_2]$, $[Fe^{III}Tp_2][TCNQ]$, $[Fe^{III}Cp_2][Fe^{III}Cb_2]$ and $[E-Fc-CH=CH-p-C_5H_4NMe][M^{III}Cb_2]$ ($M = Fe, Ni, Co$) were synthesised using metathesis reactions. The IR spectra of the dicarborollide (Cb) containing salts contained bands attributable to $\nu_{max}(BH)$ at ca. 2550 cm^{-1} . The IR spectra of salts containing the $[Fe^{III}Tp_2]^+$ ion should also contain $\nu_{max}(BH)$ at 2500 cm^{-1} , but the intensity of this band is small in comparison with that from the metal-dicarborollide anions, and it could not be separately identified in the spectra. The spectra of the methylpyridinium salts and the methylisoquinolinium salts all showed bands in the region $1400\text{--}1600\text{ cm}^{-1}$ attributed to aromatic C–H bands. The IR spectra of the ferrocenium salts similarly contained bands in the region $1400\text{--}1600\text{ cm}^{-1}$ attributable to the C–H vibrations of the cyclopentadienyl ring. In addition, $[Fe^{III}\{(OC_6H_4-4-$

$C(Me)=N(CH_2)_2NH(CH_2)_2\}_2][Fe^{III}Cb_2]$ exhibited a band at 1590 cm^{-1} assigned to $\nu_{max}(C=N)$ associated with the Schiff Base ligand. In $[Fe^{III}Tp_2][TCNQ]_2$ a band is observed at 2475 cm^{-1} attributable to $\nu_{max}(BH)$ in the Tp^- ligand. The $\nu_{C=N}$ frequency was found at 2208 cm^{-1} only slightly different from the value reported for $TCNQ^-$. The salts containing $[E-Fc-CH=CH-p-C_5H_4NMe]^+$ all displayed strong absorption bands in the region $2900\text{--}3000\text{ cm}^{-1}$ assigned to $\nu_{max}(C-H)$ and showed characteristic aromatic C–H bands in the region of $1400\text{--}1600\text{ cm}^{-1}$.

Both positive and negative ion fast atom bombardment (FAB) mass spectra were recorded from the new compounds, and in each case contained intense ions at the expected m/z values arising from the cation and the anion present. Fragments containing boron and iron show ion envelopes with intensity distributions in accordance with their expected isotopic compositions.

^{11}B NMR spectroscopy was used to confirm the presence of the dicarborollide ligand in these materials. Any substitution or degradation of the Cb cage during the preparation of the salts will result in changes in the ^{11}B NMR spectrum. However, the salts containing metal bis-dicarborollide anions gave ^{11}B NMR spectra that showed no evidence of degradation or substitution. To confirm the stoichiometry of the salts obtained, solution conductivity and electronic spectral measurements were used. The conductivities of $10^{-4}\text{ mol dm}^{-3}$ solutions of selected examples of the new salts in acetonitrile were in accord with their formulation as 1:1 electrolytes [20]. Similarly, UV–VIS spectroscopy shows that $[Fe^{III}Tp_2][Ni^{III}Cb_2]$, $[Fe^{III}Tp_2][Fe^{III}Cb_2]$, $[C_5H_5NMe][Fe^{III}Cb_2]$ and $[4-PhC_6H_4NMe][Fe^{III}Cb_2]$ are 1:1 salts, as the ratio of the extinction coefficients of the starting materials is approximately the same as the ratio of the corresponding absorption peak maxima in the final product.

In an extension of the synthetic programme, the degradation reactions of $[MCb_2]^-$ ($M = Fe, Co, Ni$) were investigated. The formation of bi- and tri-metallic metallocarborane oligomers containing three or four icosahedral units linked by cobalt centres was first described by Churchill et al. [21,22]. Subsequent studies established that the polyhedral subrogation of $[Co(Cp)(Cb)]$ by base degradation in the presence of Co^{2+} ions afforded the related compounds $[(CoCp)_2(Cn)]$ ($Cn^{4-} = C_2B_8H_{10}^{4-}$) and $[(CoCpCn)_2Co]$ [23,24]. More recent reports have suggested that higher oligomers are synthetically accessible through degradation reactions of $[CoCb_2]^-$ in the presence of Co^{2+} [25–28]. Such carborane-based metallocene analogues are possible sources of new molecular materials with potentially interesting magnetic properties. In seeking synthetic routes to paramagnetic oligomers such as $[(CoCbCn)_2M]^{3-}$ ($M = Fe, Ni, Cu$) and $[(MCbCn)_2Co]^{3-}$, we have examined the degradation of

$[\text{MCb}_2]^-$ and $[\text{CoCb}_2]^-$ in the presence of Co^{2+} or M^{2+} , respectively. Despite repeated attempts using various degradation conditions, we were unable to isolate oligomeric compounds of this type. Either the precursor $[\text{MCb}_2]^-$ was recovered unchanged or, under more forcing conditions, complete destruction of the metallocarborane occurred. The failure of these reactions prompted us to reinvestigate the degradation reactions of $[\text{CoCb}_2]^-$ itself and we were able to prepare the previously reported [21,22] bi- and trimetallic ions $\{[\text{CoCb}_2]_2(\text{Cn})\}^{2-}$ and $\{[\text{CoCbCn}]_2\text{Co}\}^{3-}$ without difficulty. However, we were unable to isolate any higher oligomers such as the tetra-metallic compound $\{[\text{CoCbCnCo}]_2\text{Cn}\}^{4-}$. In an attempt to obtain evidence for the presence of such higher oligomers in the reaction mixtures produced, NMR and mass spectrometric studies were carried out. The utility of ^{11}B NMR spectroscopy in studying these reactions is limited by signal overlap, but the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\{[\text{CoCb}_2]_2(\text{Cn})\}^{2-}$ and $\{[\text{CoCbCn}]_2\text{Co}\}^{3-}$ contain two well resolved signals corresponding with the two types of carbon environment present; one in the Cb ligand, the other in the Cn ligand. The relative integration of these two signals depends upon the extent of oligomerisation. In $[\text{Co}(\text{Cb})_2]^-$, there is a single signal at $\delta_{\text{C}}(\text{CDCl}_3) = 51.80$ ppm due to the four Cb carbons. In $\{[\text{CbCo}]_2\text{Cn}\}^{2-}$ there are two signals of relative areas 2:4 at $\delta_{\text{C}}(\text{CDCl}_3) = 56.70$ and 48.70 ppm due respectively to the Cn and Cb carbon atoms, while in $\{[\text{CoCbCn}]_2\text{Co}\}^{3-}$, these signals appear at $\delta_{\text{C}}(\text{CD}_3)_2\text{CO} = 55.32$ and 48.22 ppm but in the area ratio 4:4. In the case of $\{[\text{CoCbCnCo}]_2\text{Cn}\}^{4-}$ two signals in the area ratio 6:4 would be expected. However, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the material precipitated from the complete reaction mixtures using Me_4N^+ (TMA^+) contained signals at $\delta_{\text{C}}(\text{CD}_3)_2\text{CO} = 55.32$ and 48.22 ppm in the area ratio 3:4, implying that the major products were $\{[\text{CoCb}]_2\text{Cn}\}^{2-}$ and $\{[\text{CoCbCn}]_2\text{Co}\}^{3-}$. Chromatographic fractionation of the reaction mixture failed to provide evidence of compounds with $^{13}\text{C}\{^1\text{H}\}$ NMR signals in area ratios greater than 4:4. To obtain further information on the composition of the reaction mixture, positive and negative ion fast atom bombardment mass spectra (FABMS) were recorded. The negative ion FABMS (*m*-nitrobenzyl alcohol = NOBA matrix) of the product mixture contained a series of ion clusters based at *m/z* values of 756 (100%), 831 (14%), 906 (20%) and 1059 (6%), which may be assigned to ions derived from the $\{[\text{CbCo}(\text{Cn})]_2\text{Co}\}^{3-}$ moiety as follows: 757, $\{[\text{M3}] \cdot \text{TMA}\}^-$ $\{[\text{M3}] = \{[\text{CbCo}(\text{Cn})]_2\text{Co}\}\}$; 831, $\{[\text{M3}] \cdot (\text{TMA})_2\}^-$; 908, $\{[\text{M3}] \cdot \text{TMA} \cdot \text{NOBA}\}^-$ and 1059 $\{[\text{M3}] \cdot \text{TMA} \cdot (\text{NOBA})_2\}^-$. On the basis of these results we are unable to confirm that higher oligomers such as $\{[\text{CoCbCnCo}]_2\text{Cn}\}^{4-}$ are formed during the degradation of $[\text{CoCb}_2]^-$ in the presence of Co^{2+} .

2.2. Magnetic susceptibility measurements

The magnetic susceptibilities of microcrystalline samples of the new materials were measured at room temperature using a Johnson Matthey magnetic susceptibility balance and, in selected cases, over the temperature range 6–300 K using a Squid magnetometer. Room temperature magnetic moments [29] were found to be ca. $2.0 \mu_{\text{B}}$ for salts with one $S = 1/2$ ion and ca. $3.0 \mu_{\text{B}}$ for salts with two noninteracting $S = 1/2$ ions (Table 1). These values are slightly higher than the spin-only value expected for an isolated $S = 1/2$ ion ($1.73 \mu_{\text{B}}$) or the average spin only value expected for two noninteracting $S = 1/2$ ions ($\mu_{\text{av}} = 2.45 \mu_{\text{B}}$) and so may indicate the presence of an orbital contribution to the observed magnetic moments. The salts $[\text{C}_5\text{H}_5\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$, $[\text{C}_9\text{H}_7\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$ and $[\text{C}_{11}\text{H}_9\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$ showed simple Curie Law behaviour between 0 and 300 K. Plots of $1/\chi_{\text{m}}$ vs. T were linear and fitted the Curie–Weiss law $\{\chi_{\text{m}} = C/(T - \theta)\}$ with Weiss temperatures, θ , which were, within experimental errors, essentially zero $\{\theta = 0(\pm 1) \text{ K}\}$, indicating that significant magnetic interactions were not occurring. Similar results were obtained for $[\text{Fe}^{\text{III}}\text{Cp}_2][\text{Fe}^{\text{III}}\text{Cb}_2]$ but $[\text{Fe}^{\text{III}}\text{Tp}_2][\text{TCNQ}]$ showed simple Curie Law behaviour only between 6 and 25 K. Above this temperature, a deviation from linearity occurred with $1/\chi_{\text{m}}$ values falling below those predicted from the $1/\chi_{\text{m}}$ vs. T plot from 0 to 25 K. Single crystal magnetic susceptibility measurements were made on $[\text{Fe}^{\text{III}}\text{Cp}_2][\text{Ni}^{\text{III}}\text{Cb}_2]$ along the axis perpendicular to the *bc* plane over the temperature range 6 to 200 K. Typical paramagnetic behaviour was again observed with θ close to zero, and $\chi_{\text{v}} \rightarrow \infty$ as $T \rightarrow 0$. Some curvature was found in the $1/\chi_{\text{m}}$ vs. T plot, but as the mass of the single crystal used was only a twentieth that of the powdered sample used, and as the χ_{m} values are and near the sensitivity limit of the Squid this may result from some errors in measurement. It is apparent from these results that none of the systems studied so

Table 1
Magnetic susceptibility data

Compound	$\chi_{\text{m}}^{\text{a}}$ ($10^{-6} \text{ cm}^3 \text{ mol}^{-1}$)	$\mu_{\text{eff}}^{\text{b}}$
$[\text{Fe}^{\text{III}}\text{Cp}_2][\text{Fe}^{\text{III}}\text{Cb}_2]$	3652	3.04
$[\text{Fe}^{\text{III}}\text{Tp}_2][\text{Fe}^{\text{III}}\text{Cb}_2]$	3695	3.12
$[\text{Fe}^{\text{III}}\{(\text{aceph})_2\text{trien}\}][\text{Fe}^{\text{III}}\text{Cb}_2]$	3386	3.00
$[\text{C}_9\text{H}_7\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$	1582	2.10
$[4\text{-PhC}_5\text{H}_4\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$	1480	2.06
$[\text{C}_5\text{H}_5\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$	1530	2.03
$[\text{Fe}^{\text{III}}\text{Tp}_2][\text{TCNQ}]$	3456	3.11

^aDetermined at $T = 293$ K using a Johnson Matthey magnetic susceptibility balance.

^bCalculated from $\mu_{\text{eff}} = \sqrt{(7.997 \cdot \chi_{\text{m}}^{\text{corr}} \cdot T)}$ where $\chi_{\text{m}}^{\text{corr}}$ is obtained from χ_{m} by applying the appropriate diamagnetic correction [18].

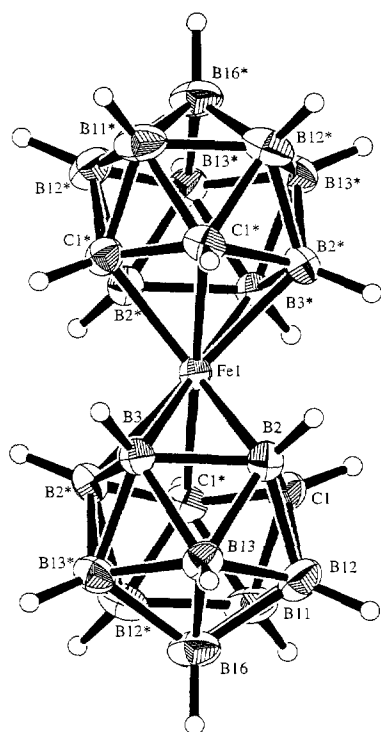


Fig. 1. View [25] of the $\text{Fe}^{\text{III}}\text{Cb}_2$ anion in the crystal structure of $[\text{MeNC}_5\text{H}_4\text{-4-Me}][\text{Fe}^{\text{III}}\text{Cb}_2]$. Ellipsoids are drawn at the 30% probability level.

far exhibit significant cooperative magnetic behaviour over the temperature range studied.

2.3. Structural studies

The crystal structure of $[4\text{-MeC}_5\text{H}_4\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$ is illustrated in Figs. 1 and 2, and atomic coordinates are listed in Table 2. The cation and anion each exhibit crystallographically imposed $2/m$ (C_{2h}) symmetry. The $[4\text{-MeC}_5\text{H}_4\text{NMe}]$ cation is, therefore, disordered, the nitrogen and opposing carbon atom being indistinguishable,¹ and the $[\text{Fe}^{\text{III}}\text{Cb}_2]^-$ anion adopts a transoid conformation. A transoid conformation of the anion is also observed in its tetrabutylammonium salt; although, in contrast in the TTF salts [15] it adopts a staggered cisoid conformation. There is one unpaired electron on the iron(III) ion, and the methylpicolinium cation is diamagnetic so that, if the aromatic portion of the cation is near enough in space to a metal-bonded C_2B_3 ring, electronic interactions in which unpaired spin may be transferred into the cation may be possible. The closest distance between the C_2B_3 ring and the aromatic ring was found to be 3.975(4) Å (B3 and N2O), which is greater than the combined van der Waals radii of nitrogen and boron, which are 1.50 Å and 1.70–1.80 Å,

¹ In the refinement, these atoms were treated as 50% C + 50% N.

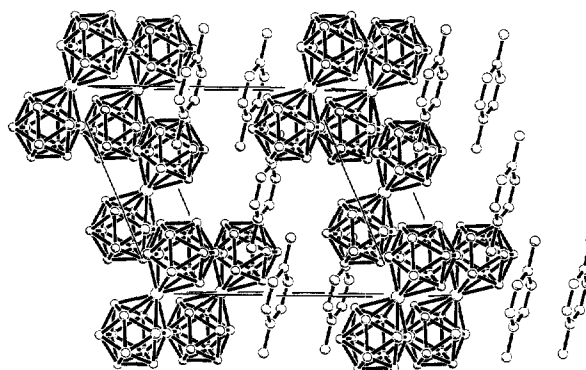


Fig. 2. The packing arrangement [26] in the crystal structure of $[\text{MeNC}_5\text{H}_4\text{-4-Me}][\text{Fe}^{\text{III}}\text{Cb}_2]$, viewed in the direction close to y ; x up the page, z across the page. Starred atoms are related to the corresponding unstarred atoms by the crystallographic symmetry.

respectively [30]. Therefore, there can be no significant orbital overlap between the anion and cation. As required by the crystallographic symmetry, the two C_2B_3 rings are parallel to one another with the carbons nearer to the metal centre, $\text{Fe}-\text{C}$ 2.080(2), $\text{Fe}-\text{B}$ (mean) 2.136(6) Å. The methylpicolinium cations do not form π -interacting stacks, the nearest cation–cation distance being greater than 5 Å.

The salt $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{Ni}^{\text{III}}\text{Cb}_2]$ was obtained directly from an electron transfer reaction between $[\text{Fe}^{\text{II}}\text{Cp}_2^*]$ and $[\text{Ni}^{\text{IV}}\text{Cb}_2]$. This compound has been reported [16] previously along with the X-ray crystal structure of its isomorphous counterpart $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{Fe}^{\text{III}}\text{Cb}_2]$. The anion and cation structures are shown in Fig. 3, and the packing arrangement in Fig. 4. Atomic coordinates are in Table 3. As was found [16] in the iron analogue, the two carborane ligands are twisted with respect to each other by ca. 108° . Each of the two C_2B_3 rings is planar to within ± 0.03 Å and the rings are almost parallel to one another [interplanar angle $2.3(2)^\circ$], with the carbons again slightly nearer to the metal centre in each ring [mean distances $\text{Ni}-\text{C}$ 2.124(17), $\text{Ni}-\text{B}$ 2.134(9) Å. The

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[\text{Me}_2\text{-C}_5\text{H}_4\text{N}][\text{FeCb}_2]$

	x	y	z	U_{eq}
Fe(1)	0	0	0	37(1)
C(1)	1909(2)	812(2)	538(2)	52(1)
B(2)	1077(2)	1426(2)	1372(2)	48(1)
B(3)	539(3)	0	1960(2)	42(1)
B(11)	3380(3)	0	1400(3)	69(1)
B(12)	2857(2)	1429(3)	1971(2)	65(1)
B(13)	2023(2)	883(2)	2902(2)	53(1)
B(16)	3446(3)	0	2913(3)	69(1)
N(20)	-1341(2)	0	4233(2)	54(1)
C(21)	-665(2)	-1171(2)	4623(2)	55(1)
C(22)	-2784(3)	0	3419(4)	86(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

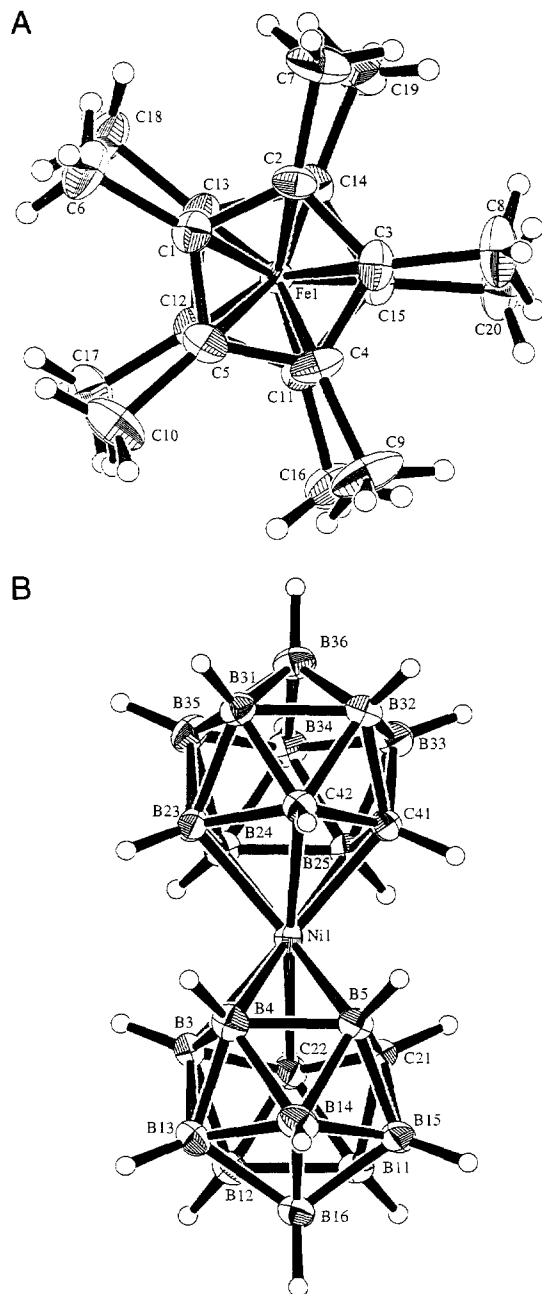


Fig. 3. View [25] of (a) the $[\text{Fe}^{\text{III}}\text{Cp}_2^*]^+$ cation and (b) the $[\text{Ni}^{\text{III}}\text{Cb}_2]^-$ anion in the crystal structure of $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{Ni}^{\text{III}}\text{Cb}_2]$.

$[\text{FeCp}_2^*]^+$ cations have planar cyclopentadienyl rings (maximum deviations from planarity ± 0.003 Å with the methyl groups displaced by 0.07–0.09 Å from their respective rings in a direction away from the central Fe atom. The rings are essentially parallel [interplanar angle $1.0(1)^\circ$], and are twisted relative to one another by ca. 10° from an eclipsed conformation. The Fe–C distances average 2.095(3) Å to the C(1)–C(5) ring and 2.103(2) Å to the C(11)–C(15) ring. Interestingly, in the isomorphous $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{Fe}^{\text{III}}\text{Cb}_2]$, the cyclopentadienyl rings are eclipsed [16].

The anion and cation pack as predicted (Fig. 4), as the faces of the Cp^* rings are almost perpendicular to those of the C_2B_3 rings of the dicarbollide ligands [interplanar angles in the range 88.1 – 89.75°]. The atoms C(3), C(15), Fe(1), B(3), B(4), B(5), C(21) and C(22) are coplanar to within ± 0.04 Å. The salt has an anisotropic structure, with anion and cation pairs along the a -axis showing a smaller separation than those along the c -axis (Fig. 4). The nearest neighbour anion/cation ring distance is 3.722(5) Å (B4 and C3), so there can be no significant π – π orbital overlap between the anion and cation. This is also the case in Miller's salts where the anion–cation separation is great enough that there is no significant π – π orbital overlap. Since magnetic properties are a consequence of spin–spin interactions, and the dominant spins in the salt $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{Ni}^{\text{III}}\text{Cb}_2]$ reside on the two metal centres, which each have an unpaired electron, it is these distances that are deemed to be the vital factor in the process of virtual charge transfer, which stabilises ferromagnetic or antiferromagnetic coupling.

The closest separation of the Fe(III) and Ni(III) metal centres is 7.106(1) Å, which is greater than the 5.6-Å found between Fe(III) and the nearest $[\text{TCNE}]^-$ nitrogen atom in $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{TCNE}]$ [12]. The lack of any significant cooperative behaviour may be due to the large separation of the paramagnetic centres. However, ^{11}B and ^{13}C NMR studies of metallobisdicarbollides have revealed some small delocalisation of the unpaired spin from the metal centre to the C_2B_3 bonding face [14]. Thus, for the unpaired spins on $[\text{Fe}^{\text{III}}\text{Cp}_2^*]^+$ and $[\text{Ni}^{\text{III}}\text{Cb}_2]^-$ to interact, the distances must be short enough for significant orbital overlap between the Fe(III) metal centre and the C_2B_3 ring. The closest Fe(III)– C_2B_3 distances, Fe...B(25) 5.526(4), Fe...B(4) 5.531(4) Å, are now comparable to those found in Miller's ferromagnetic molecular salts. The lack of any magnetic cooperation in the salts $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{Ni}^{\text{III}}\text{Cb}_2]$ and $[\text{TTF}][\text{Cr}^{\text{III}}\text{Cb}_2]$ prepared by Forward et al. [15,16], suggests that distance criteria alone do not provide an

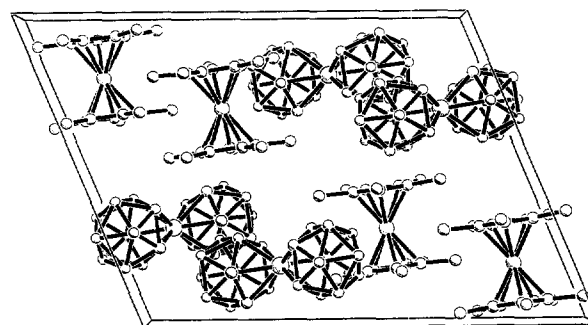


Fig. 4. The packing arrangement [26] in the crystal structure of $[\text{Fe}^{\text{III}}\text{Cp}_2^*][\text{Ni}^{\text{III}}\text{Cb}_2]$, viewed along y ; x up the page, z across the page.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[\text{FeCp}_2][\text{NiCb}_2]$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ni(1)	3098(1)	2254(1)	1449(1)	29(1)
Fe(1)	8043(1)	1751(1)	1287(1)	28(1)
C(21)	2439(2)	3553(2)	952(2)	34(1)
C(22)	1906(2)	2676(2)	389(2)	42(1)
C(41)	3310(2)	2488(2)	2609(2)	35(1)
C(42)	4278(2)	1948(2)	2539(2)	39(1)
B(3)	2834(3)	1970(3)	281(2)	41(1)
B(4)	4041(3)	2569(3)	806(2)	43(1)
B(5)	3716(3)	3566(3)	1237(2)	38(1)
B(11)	1803(3)	3809(3)	-4(2)	45(1)
B(12)	2085(3)	2795(3)	-456(2)	48(1)
B(13)	3425(3)	2740(3)	-198(2)	49(1)
B(14)	3958(3)	3749(3)	397(2)	49(1)
B(15)	2964(3)	4375(3)	540(2)	45(1)
B(16)	2780(3)	3878(3)	-376(2)	49(1)
B(23)	3861(3)	970(2)	1937(2)	38(1)
B(24)	2488(3)	916(3)	1683(2)	41(1)
B(25)	2202(3)	1927(3)	2119(2)	38(1)
B(31)	4442(3)	859(3)	2966(2)	42(1)
B(32)	4103(3)	1859(3)	3394(2)	41(1)
B(33)	2761(3)	1846(3)	3126(2)	45(1)
B(34)	2282(3)	804(3)	2566(2)	47(1)
B(35)	3309(3)	205(3)	2445(2)	48(1)
B(36)	3475(3)	751(3)	3344(2)	49(1)
C(1)	6620(2)	1425(2)	443(2)	41(1)
C(2)	6682(2)	2415(2)	596(2)	38(1)
C(3)	6848(2)	2545(2)	1389(2)	45(1)
C(4)	6878(2)	1601(3)	1705(2)	45(1)
C(5)	6743(2)	927(2)	1122(2)	43(1)
C(6)	6393(3)	988(4)	-345(2)	72(1)
C(7)	6536(4)	3211(3)	22(3)	75(1)
C(8)	6892(4)	3476(3)	1796(3)	82(2)
C(9)	6981(3)	1374(4)	2518(2)	82(2)
C(10)	6656(4)	-150(3)	1195(3)	78(1)
C(11)	9440(2)	1389(2)	2153(2)	40(1)
C(12)	9305(2)	849(2)	1474(2)	41(1)
C(13)	9211(2)	1507(2)	870(2)	40(1)
C(14)	9285(2)	2460(2)	1171(2)	41(1)
C(15)	9429(2)	2385(2)	1961(2)	41(1)
C(16)	9622(3)	992(3)	2935(2)	63(1)
C(17)	9333(3)	-226(3)	1417(3)	62(1)
C(18)	9110(3)	1238(3)	66(2)	65(1)
C(19)	9282(3)	3376(3)	742(3)	64(1)
C(20)	9609(3)	3204(3)	2516(3)	66(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

indication of whether or not significant magnetic interactions will be present.

2.4. Kurtz powder test results

The methylpyridinium, picolinium and isoquinolinium cations are dipolar and polarisable and, if present in noncentrosymmetric crystal structures, may give rise to second-order nonlinear optical effects such as secondary harmonic generation (SHG). This possibility was investigated by carrying out Kurtz powder test measurements

for SHG on $[\text{C}_5\text{H}_5\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$, $[\text{4-PhC}_6\text{H}_4\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$, $[\text{C}_9\text{H}_7\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$ and $[\text{MeC}_5\text{H}_4\text{N-Me}][\text{Fe}^{\text{III}}\text{Cb}_2]$. Among these, only the salt $[\text{4-PhC}_5\text{H}_4\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$ exhibits SHG with an efficiency of 0.5 times urea at $1.907 \mu\text{m}$ and 0.1 times urea at $1.064 \mu\text{m}$. Single crystal X-ray studies have shown that $[\text{MeC}_5\text{H}_4\text{NMe}][\text{Fe}^{\text{III}}\text{Cb}_2]$ crystallises in a centrosymmetric space group so that the absence of SHG in this case is in accordance with the structural results. Since $[\text{E-Fc-CH}=\text{CH-}p\text{-C}_5\text{H}_4\text{NMe}]\text{I}$ exhibits a SHG intensity of 220 times urea [17], the complexes $[\text{E-Fc-CH}=\text{CH-}p\text{-C}_5\text{H}_4\text{NMe}][\text{M}^{\text{III}}\text{Cb}_2]$ ($\text{M} = \text{Fe}, \text{Co}$) were also tested for SHG, but only the $[\text{Co}^{\text{III}}\text{Cb}_2]^-$ salt was active, giving a weak but detectable signal of intensity 0.01 times urea at $1.907 \mu\text{m}$ and 0.004 times urea at $1.064 \mu\text{m}$.

3. Experimental details

3.1. Synthetic studies

Solvents were purified by distillation from standard drying agents under dinitrogen. All commercial reagents were predried and recrystallised before use, but were used as received unless otherwise stated. The reagents $\text{K}[\text{Fe}^{\text{III}}\text{Cb}_2]$, $\text{K}[\text{Ni}^{\text{III}}\text{Cb}_2]$, $[\text{Ni}^{\text{IV}}\text{Cb}_2]$ [10], LiTCNQ [31], $[\text{Fe}^{\text{III}}\{\text{C}_6\text{H}_4(\text{OH})\text{C}(\text{R})=\text{N}(\text{CH}_2)_2\text{NHCH}_2\}_2]\text{PF}_6$, ($\text{R} = \text{H}, \text{Me}$), [13b] $[\text{Fe}^{\text{III}}\text{Tp}_2]\text{Cl}$ [13b] and $[\text{E-Fc-CH}=\text{CH-}p\text{-C}_5\text{H}_4\text{NMe}]\text{I}$ [17] were prepared according to reported methods.

3.2. Physical measurements

IR spectra were recorded from KBr discs using a Perkin Elmer 1600 series FT-IR spectrophotometer, ^{11}B NMR spectra from dichloromethane solutions using a Jeol GX270 spectrometer, and positive or negative ion mass spectra from a 3-nitrobenzyl alcohol (NOBA) matrix using a Kratos MS80 instrument with fast atom bombardment. Room temperature magnetic susceptibilities and magnetic moments were determined using a Johnson Matthey magnetic susceptibility balance. Magnetic susceptibility data was also collected over the temperature range 6–275 K using a Squid magnetometer in the School of Physics, University of Birmingham. Solution conductivity measurements were recorded from $1 \times 10^{-4} \text{ mol dm}^{-3}$ solutions in MeCN using a PTI 58 digital conductivity meter. The determination of the second harmonic intensity of powder samples was made relative to that of powdered urea. Pulses (width 4 ns, repetition rate 1 Hz) of 0.2 mJ energy at a wavelength of $1.907 \mu\text{m}$ were weakly focused into sample cells containing finely ground (ungraded) material, and the second harmonic light at 950 nm measured on an S1 photomultiplier tube. Boxcar gate sampling was used to

provide data points averaged over 10 pulses and the mean of these points provided the values of relative harmonic intensity for SHG quoted. Elemental analyses were performed by the Microanalytical Service, School of Chemistry, University of Birmingham and the Microanalytical Service, School of Chemistry, University of Sheffield.

3.3. $[Fe^{III}Tp_2][Fe^{III}Cb_2]$

$K[Fe^{III}Cb_2]$ (0.43 g, 1.2 mmol) was dissolved in deionised water (20 cm³) and the solution added dropwise to a solution of $[Fe^{III}Tb_2]Cl$ (0.52 g, 1.0 mmol) in acetone (2 cm³) and the mixture stirred vigorously for 30 min, during which time a red precipitate was formed. This was collected by filtration and washed with deionised water (200 cm³) followed by hexane (20 cm³) then dried in vacuo. The solid obtained was recrystallised twice from dichloromethane/hexane (50:50) to yield a red crystalline product (0.771 g, 97%). (Found: C, 33.3; H, 5.21; N, 21.1. $C_{22}H_{42}N_{12}B_{18}Fe_2$, requires, C, 32.9; H, 5.27; N, 21.1%): $\nu_{max}(BH)$ 2535 cm⁻¹; mass spectrum m/z ($I\%$): +ve FAB, 482 (100) [M^+]; -ve FAB, 321 (16) [M^-], 153 (100) [NOBA⁻]; A_m , 156 Ω cm² mol⁻¹.

3.4. $[Fe^{III}\{C_6H_4(O)C(Me)=N(CH_2)_2NHCH_2\}_2][Fe^{III}Cb_2]$

The procedure described above for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ was followed, using $K[Fe^{III}Cb_2]$ (0.43 g, 1.2 mmol) and $[Fe^{III}\{C_6H_4(O)C(Me)=N(CH_2)_2NHCH_2\}_2]PF_6$ (0.58 g, 1.0 mmol). A red crystalline solid was formed (0.715 g, 95%). (Found: C, 40.9; H, 6.54; N, 7.26. $C_{26}H_{50}N_4O_2B_{18}Fe_2$, requires, C, 41.3; H, 6.66; N, 7.40%): $\nu_{max}(BH)$ 2538.2 cm⁻¹, $\nu_{max}(C=N)$ 1591.2 cm⁻¹; $^{11}B\{^1H\}$ (CH_2Cl_2) δ ; 83.74 ppm (2B), 2.11 ppm (4B), -18.99 ppm (4B), -52.01 ppm (2B), -428.67 ppm (4B), -479.32 ppm (2B); mass spectrum m/z ($I\%$): +ve FAB, 436 (100), 288 (20), 245 (17); -ve FAB, 321 (100) 153 (45); A_m , 182 Ω cm² mol⁻¹.

3.5. $[C_9H_7NMe][Fe^{III}Cb_2]$

The procedure described for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ was followed using $K[Fe^{III}Cb_2]$ (0.43 g, 0.12 mmol) and $[C_9H_7N-Me]I$ (0.27 g, 1.0 mmol). A red crystalline solid was formed (0.446 g, 96%). (Found: C, 36.0; H, 6.76; N, 2.95. $C_{14}H_{32}NB_{18}Fe$, requires, C, 36.2; H, 6.94; N, 3.01%): $\nu_{max}(BH)$ 2551s cm⁻¹; $^{11}B\{^1H\}$ (CH_2Cl_2) δ ; 85.24 ppm (2B), 2.42 ppm (4B), -19.01 ppm (4B), -51.70 ppm (2B), -428.00 ppm (4B), -477.65 ppm (2B); mass spectrum m/z ($I\%$): +ve FAB, 144 (100) [M^+], 107 (22), 89 (30); -ve FAB, 321 (100) [M^-], 153 (58).

3.6. $[4-MeC_5H_4NMe][Fe^{III}Cb_2]$

The procedure described for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ was followed using $K[Fe^{III}Cb_2]$ (0.43 g, 1.2 mmol) and $[Me-C_9H_7N-Me]I$ (0.11 g, 1.0 mmol). A red crystalline solid was formed (0.42 g, 98%). (Found: C, 30.8; H, 7.47; N, 3.39. $C_{11}H_{32}NB_{18}Fe$, requires, C, 30.8; H, 7.52; N, 3.27%): $\nu_{max}(BH)$ 2546s cm⁻¹; $^{11}B\{^1H\}$ (CH_2Cl_2) δ ; 83.67 ppm (2B), 2.00 ppm (4B), -19.65 ppm (4B), -50.92 ppm (2B), -428.55 ppm (4B), -477.81 ppm (2B); mass spectrum m/z ($I\%$): +ve FAB, 108 (100) [M^+], 93 (30) [M^+-Me]; -ve FAB, 321 [M^-] (100), 153 (58); A_m , 174 Ω cm² mol⁻¹.

3.7. $[C_5H_5NMe][Fe^{III}Cb_2]$

The procedure described for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ was followed using $K[Fe^{III}Cb_2]$ (0.43 g, 1.2 mmol) and $[C_5H_5N-Me]I$ (0.22 g, 1.0 mmol). A red crystalline solid was formed (0.394 g, 95%). (Found: C, 28.9; H, 7.31; N, 3.34. $C_{10}H_{30}NB_{18}Fe$, requires, C, 29.0; H, 7.29; N, 3.38%): $\nu_{max}(BH)$ 2534s cm⁻¹; $^{11}B\{^1H\}$ (CH_2Cl_2) δ ; 85.22 ppm (2B), 2.44 ppm (4B), -18.87 ppm (4B), -50.73 ppm (2B), -426.36 ppm (4B), -476.28 ppm (2B); mass spectrum m/z ($I\%$): +ve FAB, 94 (100) [M^+]; -ve FAB, 321 (100) [M^-], 153 (78).

3.8. $[4-PhC_6H_4NMe][Fe^{III}Cb_2]$

The procedure described for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ was followed using $K[Fe^{III}Cb_2]$ (0.43 g, 1.2 mmol) and $[C_{11}H_{10}N-Me]I$ (0.30 g, 1.0 mmol). A red crystalline solid was formed (0.457 g, 93%). (Found: C, 39.0; H, 7.01; N, 2.39. $C_{16}H_{34}NB_{18}Fe$, requires, C, 39.2; H, 6.98; N, 2.85%): $\nu_{max}(BH)$ 2539s cm⁻¹; $^{11}B\{^1H\}$ (CH_2Cl_2) δ ; 85.76 ppm (2B), 2.53 ppm (4B), -18.87 ppm (4B), -51.90 ppm (2B), -428.44 ppm (4B), -478.90 ppm (2B); mass spectrum m/z ($I\%$): +ve FAB, 170 (100) [M^+]; -ve FAB, 321 (34) [M^-].

3.9. $[Fe^{III}Tp_2][TCNQ]$

LiTCNQ (0.21 g, 1.0 mmol) was dissolved in acetonitrile (40 cm³) and added dropwise to a solution of $[Fe^{III}Tp_2]Cl$ (0.52 g, 1.0 mmol) in acetonitrile (60 cm³). A dark blue precipitate formed from the green solution and this was collected by filtration. The solid was washed with diethylether, water (30 cm³) and hexane (20 cm³). Further purification was achieved by recrystallisation from acetonitrile to yield a dark blue crystalline material (0.033 g, 62%). (Found: C, 56.6; H, 3.9; N, 30.4. $C_{42}H_{28}N_{12}Fe$, requires, C, 56.7; H, 3.2; N, 31.5): $\nu_{max}(BH)$ 2475m, $\nu_{max}(CN)$ 2208m cm⁻¹; mass spectrum m/z ($I\%$): +ve FAB, 482 (100) [M^+], 415 (42) [M^+-Pz], 269 (61) [M^+-Tp]; -ve FAB, 204 (100)

$[M^-]$, 166 (28) $[M^- - CNC]$, 153 (50); A_m , 177 $\Omega \text{ cm}^2 \text{ mol}^{-1}$.

3.10. $[Fe^{III}Cp_2][Fe^{III}Cb_2]$

$K[Fe^{III}Cb_2]$ (0.43 g, 1.2 mmol) was dissolved in deionised water (10 cm^3) and the solution added dropwise to an aqueous solution of $[Fe^{III}Cp_2]_2SO_4$ (0.50 g, 1.1 mmol). The solution was treated as for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ to yield a red solid (0.615 g, 95%). (Found: C, 32.7; H, 6.18; N, 0.00. $C_{14}H_{32}B_{18}Fe_2$, requires, C, 33.2; H, 6.37; N, 0.00%): $\nu_{\max}(\text{BH})$ 2536s cm^{-1} ; $^{11}\text{B}\{^1\text{H}\}$ (CH_2Cl_2) δ ; 85.76 ppm (2B), 3.44 ppm (4B), -18.87 ppm (4B), -50.73 ppm (2B), -426.36 ppm (4B), -476.28 ppm (2B); mass spectrum m/z ($I\%$); +ve FAB, 186 (100) $[M^+]$; 136 (66); -ve FAB, 321 (100) $[M^-]$, 153 (60); A_m , 140 $\Omega \text{ cm}^2 \text{ mol}^{-1}$.

3.11. $[Fe^{III}Cp_2^*][Ni^{III}Cb_2]$

$[Fe^{III}Cp_2^*]$ (0.10 g, 0.31 mmol) was dissolved in acetonitrile (10 cm^3), under an inert atmosphere, and a solution of $[Ni^{III}Cb_2]$ (0.10 g, 0.31 mmol) in acetonitrile (10 cm^3) was added dropwise over a 15-min period. A colour change from yellow to green was immediately observed. The solution was left overnight, under an inert atmosphere, to yield large dark green rhombohedral crystals (0.189 g, 95%). The crystals were stored in a Schlenk tube under argon. (Found: C, 44.1; H, 7.99; N, 0.00. $C_{24}H_{52}B_{18}FeNi$, requires, C, 44.4; H, 8.07; N, 0.00%): $\nu_{\max}(\text{BH})$ 2572s cm^{-1} , 2546.8s cm^{-1} ; $^{11}\text{B}\{^1\text{H}\}$ (CH_2Cl_2) δ ; 4.44 ppm (2B), 1.97 ppm (4B), -12.50 ppm (4B), -14.01 ppm (2B), -24.43 ppm (4B), -34.08 ppm (2B); mass spectrum m/z ($I\%$); +ve FAB, 326 (100) $[M^+]$; -ve FAB, 323 (100) $[M^-]$; A_m , 145 $\Omega \text{ cm}^2 \text{ mol}^{-1}$.

3.12. $K[Co^{III}Cb_2]$ degradation reactions

Mixtures of $KCbH$ or $K[Co^{III}Cb_2]$ with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were degraded in aqueous NaOH solution following the general procedures described previously [25–28]. The reaction products were precipitated by adding an aqueous solution of Me_4NCl and the material obtained investigated using FABMS, ^{11}B and ^{13}C NMR techniques. A typical procedure follows.

A sample of $K[Co^{III}Cb_2]$ (1.0 g, 2.75 mmol) was dissolved in aqueous sodium hydroxide solution (30 cm^3 40% w/v) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.5 g, 4.2 mmol) added. The mixture was heated under reflux for 7 h, cooled and hydrochloric acid added until the solution became ca. pH 3. A solution of Me_4NCl (0.5 g, 4.6 mmol) dissolved in the minimum amount of water was added, and the resulting precipitate collected by filtration and washed with water. The red-brown solid was

redissolved in acetone, filtered and the filtrate evaporated to dryness in vacuo (yield 0.37 g). Column chromatography on silica gel with ethanol/hexane 1/1 v/v as the eluent afforded an orange band found to be $\text{Me}_4\text{N}[Co^{III}Cb_2]$, (-ve FABMS m/z 321, M^-). A second, red, band was eluted using acetone/ethanol 1/1 v/v and found to be $[\text{Me}_4\text{N}]_3[(\text{CbCoCn})_2\text{Co}]$ {-ve FABMS m/z 983 (17%), $[M \cdot (\text{Me}_4\text{N})_2 \cdot \text{NOBA}]^-$; 906 (22%), $[M \cdot \text{Me}_4\text{N} \cdot \text{NOBA} \cdot \text{H}]^-$; 831 (45%), $[M \cdot (\text{Me}_4\text{N})_2]^-$; 756 (100%), $[M \cdot (\text{Me}_4\text{N}) \cdot \text{H}]^-$. No further products could be isolated.

3.13. $[E\text{-Fc-CH} = \text{CH-}p\text{-C}_5\text{H}_4\text{NMe}][Fe^{III}Cb_2]$

The procedure described for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ was followed using $K[Fe^{III}Cb_2]$ (0.43 g, 0.12 mmol) and $[E\text{-Fc-CH} = \text{CH-}p\text{-C}_5\text{H}_4\text{NMe}]I$ (0.43 g, 1.0 mmol). A red crystalline solid was formed (0.61 g, 98%). (Found: C, 42.7; H, 6.87; N, 2.62. $C_{22}H_{40}NB_{18}Fe_2$, requires, C, 42.3; H, 6.45; N, 2.24%): $\nu_{\max}(\text{BH})$ 2550s cm^{-1} ; $^{11}\text{B}\{^1\text{H}\}$ (CH_2Cl_2) δ ; 85.49 ppm (2B), 3.05 ppm (4B), -19.05 ppm (4B), -50.38 ppm (2B), -425.84 ppm (4B), -478.64 ppm (2B); mass spectrum m/z ($I\%$); +ve FAB, 304 (100) $[M^+]$, 289 (7) $[M^+ - \text{Me}]$; -ve FAB, 321 (100) $[M^-]$, 153 (51); A_m , 164 $\Omega \text{ cm}^2 \text{ mol}^{-1}$.

3.14. $[E\text{-Fc-CH} = \text{CH-}p\text{-C}_5\text{H}_4\text{NMe}][Ni^{III}Cb_2]$

The procedure described for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ was followed using $K[Ni^{III}Cb_2]$ (0.43 g, 0.12 mmol) and $[E\text{-Fc-CH} = \text{CH-}p\text{-C}_5\text{H}_4\text{NMe}]I$ (0.42 g, 1.0 mmol). A red crystalline solid was formed (0.60 g, 96%). (Found: C, 41.8; H, 6.49; N, 2.23. $C_{22}H_{40}NB_{18}FeNi$, requires, C, 42.1; H, 6.42; N, 2.23%): $\nu_{\max}(\text{BH})$ 2532s cm^{-1} ; $^{11}\text{B}\{^1\text{H}\}$ (CH_2Cl_2) δ ; 86.25 ppm (2B), 2.12 ppm (4B), -18.53 ppm (4B), -51.99 ppm (2B), -426.45 ppm (4B), -478.07 ppm (2B); mass spectrum m/z ($I\%$); +ve FAB, 304 (100) $[M^+]$, 289 (7) $[M^+ - \text{Me}]$; -ve FAB, 323 (100) $[M^-]$; A_m , 155 $\Omega \text{ cm}^2 \text{ mol}^{-1}$.

3.15. $[E\text{-Fc-CH} = \text{CH-}p\text{-C}_5\text{H}_4\text{NMe}][Co^{III}Cb_2]$

The procedure described for $[Fe^{III}Tp_2][Fe^{III}Cb_2]$ was followed using $K[Co^{III}Cb_2]$ (0.43 g, 0.12 mmol) and $[E\text{-Fc-CH} = \text{CH-}p\text{-C}_5\text{H}_4\text{NMe}]I$ (0.42 g, 1.0 mmol). A red crystalline solid was formed (0.56 g, 90%). (Found: C, 42.0; H, 6.55; N, 2.16. $C_{22}H_{40}NB_{18}FeCo$, requires, C, 42.1; H, 6.42; N, 2.23%): $\nu_{\max}(\text{BH})$ 2529s cm^{-1} ; $^{11}\text{B}\{^1\text{H}\}$ (CH_2Cl_2) δ ; -12.24 ppm (2B), -18.06 ppm (4B), -22.64 ppm (4B), -24.92 ppm (4B), -37.46 ppm (2B), -42.05 ppm (2B); mass spectrum m/z ($I\%$); +ve FAB, 304 (100) $[M^+]$, 289 (7) $[M^+ - \text{Me}]$; -ve FAB, 324 (100) $[M^-]$; A_m , 181 $\Omega \text{ cm}^2 \text{ mol}^{-1}$.

3.16. Structural studies

[Fe^{III}Cp₂*][Ni^{III}Cb₂]: C₂₀H₃₀Fe · C₄H₂₂B₁₈Ni, *M_r* = 649.8, monoclinic, space group *P*2₁/*n*, *a* = 14.201(16), *b* = 13.892(12), *c* = 18.723(6) Å, β = 111.80(5)°, *V* = 3430 Å³, *Z* = 4, *D_c* = 1.258 g cm⁻³, *F*(000) = 1360, μ(Mo–Kα) = 0.990 mm⁻¹, λ = 0.71069 Å. Unit cell dimensions and intensities were determined by ω/2θ scans with graphite-monochromated Mo–Kα radiation on an Enraf-Nonius CAD-4 diffractometer. 5888 unique reflections were measured in the range 2 < θ < 25°. Three standard reflections measured every 2 h showed only small random variation in intensity during the period of data collection. The structure was determined [32] by direct methods and refined [33] on *F*² by least-squares using anisotropic displacement parameters for the nonhydrogen atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms.² Weights, *w* = 1/[σ²(*F_o*²) + (0.0464*P*)² + 4.50*P*], where *P* = (*F_o*² + 2*F_c*²)/3, were used in the least-squares refinement. The calculations were terminated when all shift/esd ratios were < 0.05 and *R* = 0.0529, *R_w* = 0.2307. For the 5210 observed reflections [*I* > 2σ(*I*)], *R* = 0.0395, *R_w* = 0.1026. The residual electron density in a final difference map was within the range ±0.45 e Å⁻³.

[4-MeC₅H₄NMe][Fe^{III}Cb₂]: C₇H₁₀N · C₄H₂₂B₁₈Fe. *M_r* = 428.8, monoclinic, space group *C*2/*m*, *a* = 10.882(4), *b* = 9.982(4), *c* = 11.836(5) Å, β = 113.42(3)°, *V* = 1180 Å³, *Z* = 2, *D_c* = 1.207 g cm⁻³, *F*(000) = 442, μ(Mo–Kα) = 0.640 mm⁻¹, λ = 0.71069 Å. Data were collected on a Rigaku R-Axis II area-detector diffractometer using graphite monochromated MoKα radiation. Twenty-six 7° oscillation exposures were made with crystal to detector distances of 80 mm. 1095 reflections, 3.75 < θ < 25.2°, having *I* > σ(*I*), were used in the analysis. The structure was determined [34] by direct methods and refined [32] on *F*² by least squares using anisotropic displacement parameters for the non-hydrogen atoms. H atoms were placed in calculated positions [33]. Refinement was terminated when all shift/esd. ratios were < 0.01 and *R*, *R_w* were 0.0342, 0.0970, respectively with *w* = 1/[σ²(*F_o*²) + (0.074*P*)² + 0.50*P*]. The residual electron density was within the range ±0.30 e Å⁻³.

For both structures [35,36], the cage carbon atoms were identified in the first instance by these atoms having slightly lower apparent thermal parameters when all cage atoms were assigned scattering factors appropriate to boron. Confirmation of the assignment was

provided by a consideration of C–C, C–B and B–B bond lengths; 1.605–1.621 Å, 1.685–1.723 Å and 1.747–1.829 Å respectively, in our structures, in good agreement with literature values of 1.659 [37], 1.716 [38] and 1.775 Å [38], respectively for these types of bonds.³

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References

- [1] J.S. Miller, A.J. Epstein, W.M. Reiff, *Chem. Rev.* 88 (1988) 201.
- [2] J.S. Miller, A.J. Epstein, W.M. Reiff, *Acc. Chem. Res.* 40 (1988) 240.
- [3] O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, O. Khan, *Science* 261 (1993) 447.
- [4] O. Kahn, Y. Pei, Y. Journaux, in: D.W. Bruce, D. O'Hare (Eds.), *Inorg. Mat.*, Wiley, Chichester, 1992, pp. 59–114.
- [5] H.M. McConnell, *J. Chem. Phys.* 39 (1963) 1910.
- [6] H.M. McConnell, *Proc. R.A. Welch Found. Conf.* 11 (1967) 144.
- [7] R. Breslow, B. Jaun, R.Q. Klutcz, C.Z. Xia, *Tetrahedron* 38 (1982) 863.
- [8] J.S. Miller, A.J. Epstein, *J. Am. Chem. Soc.* 109 (1987) 3850.
- [9] C. Collmar, O. Kahn, *J. Am. Chem. Soc.* 113 (1991) 7987.
- [10] M.F. Hawthorne, D.C. Young, T.D. Andrews, D.V. Thorne, R.L. Pilling, A.D. Pitts, M. Reintjes, L.F. Warren Jr., P.A. Wegner, *J. Am. Chem. Soc.* 90 (1968) 879.
- [11] W.E. Geiger, in: R.N. Grimes (Ed.), *Metal Interactions with Boron Clusters*, Plenum, New York, 1983.
- [12] J.S. Miller, J.C. Calabrese, H. Römmelmann, S.R. Chittipeddi, J.H. Zhang, W.M. Reiff, A.J. Epstein, *J. Am. Chem. Soc.* 109 (1987) 769.
- [13] L.F. Warren, M.F. Hawthorne, *J. Am. Chem. Soc.* 92 (1970) 1157.
- [14] R.J. Wiersema, M.F. Hawthorne, *J. Am. Chem. Soc.* 96 (1974) 761.
- [15] J.M. Forward, D.M.P. Mingos, T.E. Muller, D.J. Williams, Y.-K. Yan, *J. Organomet. Chem.* 467 (1994) 207.
- [16] J.M. Forward, D.M.P. Mingos, A.V. Powell, *J. Organomet. Chem.* 467 (1994) 251.
- [17] S.R. Marder, J.W. Perry, B.G. Tiernann, W.P. Schaefer, *Organometallics* 10 (1991) 1896.
- [18] J.L. Burmeister, S.D. Patterson, E.A. Deardoff, *Inorg. Chim. Acta* 3 (1967) 105.

² With isotropic displacement parameters of 1.2 times the *U_{eq}* value of the parent atom, except for the methyl H-atoms where a multiplication factor of 1.5 was used.

³ Supporting information available: Crystal and refinement details, anisotropic displacement parameters, hydrogen atom parameters and complete bond lengths and angles for the two structures.

- [19] A.S. Rothin, H.J. Banbery, F.J. Berry, T.A. Hamor, C.J. Jones, J.A. McCleverty, *Polyhedron* 8 (1989) 491.
- [20] W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81.
- [21] M.R. Churchill, K. Gold, J.N. Francis, M.F. Hawthorne, *J. Am. Chem. Soc.* 91 (1969) 1222.
- [22] M.R. Churchill, A.H. Reis, J.N. Francis, M.F. Hawthorne, *J. Am. Chem. Soc.* 92 (1970) 4993.
- [23] C.J. Jones, M.F. Hawthorne, *Inorg. Chem.* 12 (1973) 608.
- [24] W.E. Geiger, in: R.N. Grimes (Ed.), *Metal Interactions with Boron Clusters*, Plenum, New York, 1983.
- [25] V.V. Volkov, S. Ya Dvurechenskaya, *Koord. Khim.* 8 (1982) 263.
- [26] S. Ya Dvurechenskaya, V.V. Volkov, S.V. Trkachev, L.S. Denkina, *Zh. Neorg. Chim.* 27 (1982) 1740.
- [27] S. Ya Dvurechenskaya, V.V. Volkov, I.I. Gorbacheva, N.D. Krivosheeva, *Izv. Sib. Otd. Acad. Nauk. SSSR, Ser. Khim. Nauk.* (1983) 74.
- [28] V.V. Volkov, V.N. Ikorskii, *Izv. Acad. Nauk. SSSR, Ser. Khim.* (1983) 252.
- [29] C.J. O'Connor, *Prog. Inorg. Chem.* 29 (1982) 203.
- [30] J. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [31] L.R. Melby, R.J. Harder, W.R. Hertler, W. Mahler, R.E. Benson, W.E. Mochel, *J. Am. Chem. Soc.* 84 (1962) 3374.
- [32] G.M. Sheldrick, *Acta Crystallogr. A* 46 (1990) 467.
- [33] G.M. Sheldrick, *SHELXL-93: Program for Crystal Structure Refinement*, Univ. of Gottingen, 1993.
- [34] *Molecular Structure, TeXsan. Single Crystal Structure Analysis Software*, version 1.6. MSC, 3200 Research, Forest Drive, TX 77381, USA, 1993.
- [35] C.K. Johnson, *ORTEP. Report ORNL-5138*, Oak Ridge Natl. Lab., Oak Ridge, TN, USA, 1976.
- [36] J.W. Lauher, *CHARON: Graphics Program for Postscript Printers*, Res. Foundation of the State Univ. of New York, 1989.
- [37] *Mean of 104 Values Extracted from the Cambridge Structural Database*. Cambridge Crystallographic Data Centre, Cambridge CB2 1EZ, UK, 1996.
- [38] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* (1987) 51.