

## Magnetic and spectroscopic studies of ferricenium tetrabromoferrate(III), $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$ , a soft ferromagnet and its iodo analogue

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Detailed studies of the properties of ferricenium tetrabromoferrate (III) using electron paramagnetic resonance (EPR) and Mössbauer spectroscopy reveal that this material undergoes a magnetic transition at 13.2 K. The origin of this transition has been traced to the near neighbor ferrimagnetic coupling as evidenced by a broadening and the subsequent disappearance of an EPR line due to the  ${}^6A_1$  ground state of  $\text{FeBr}_4^-$  and an appearance of the Zeeman split Mössbauer spectrum, the latter in concurrence with earlier reports. Infrared spectrum shows the emergence of new bands around the magnetic ordering temperature. Detailed magnetization measurements as a function of temperature and field clearly indicate long range ferromagnetic ordering at a temperature below 4 K. This is corroborated by Mössbauer results with the appearance of another transition and a six line pattern due to the ferricenium cation at 2.9 K. The mechanism for ferromagnetic coupling is discussed. The change in EPR line-width and the appearance of two new EPR lines below 20 K give additional evidence to the other experimental observations. The EPR, Mössbauer and IR studies suggest that no such ordering exists in the analogous  $\text{C}_{10}\text{H}_{10}\text{Fe}_2\text{I}_4$ , probably due to a structural transition at low temperature hindering magnetic ordering.

### Introduction

As a result of the recent interest in preparing molecular based ferromagnetic materials, there have been many attempts to make ionic molecular solids comprised linear chains of alternating  $S=1/2$  metallocenium donors (D) and  $S=1/2$   $\pi$ -electron acceptors (A). Examples of acceptors include 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)<sup>1,2</sup>. Most of these donor-acceptor complexes, usually of  $D^+A^-$  type, are found to exhibit co-operative magnetic phenomena—antiferro, ferro, ferri and metamagnetism<sup>3-5</sup>. Such is the interest in the metallocenium based charge-transfer (CT) salts that there have been at least two reviews<sup>6,7</sup> on this subject, with a comprehensive look at both the organometallic and organic ferromagnets. The long range spin correlation in a complex like  $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+[\text{TCNE}]^-$  makes it ferromagnetic though such ordering takes place at very low temperatures. However, the corresponding TCNQ<sup>-</sup> complex is a metamagnet<sup>8</sup>. Changing the cation to chromocenium to form  $[\text{Cr}(\text{C}_5\text{Me}_5)_2]^+[\text{TCNE}]^-$

creates a ferrimagnet due to antiferromagnetic alignment of differing spin moments in the two centers. It is indeed interesting to note that a Prussian blue analog is one of the highest transition temperature ( $T_c$ ) molecular ferromagnetic materials<sup>9</sup>.

The ferromagnetic chain with short range order followed by long range ferromagnetic spin correlation could be achieved by alternating a high spin ion such as  $\text{Mn}^{2+}$  and a low spin metal ion or an organic free radical. Notable results were obtained by Kahn and his group<sup>10</sup> by capturing two different metal ions such as  $\text{Mn}^{2+}$  ( $S=5/2$ ) and  $\text{Cu}^{2+}$  ( $S=1/2$ ) using a single organic moiety. Instead, Gatteschi and co-workers<sup>11</sup> alternated a nitroxide radical ( $S=1/2$ ) and a manganese (II) ( $S=5/2$ ) complex. Molecular based ferro- or ferrimagnets have also been made out of systems having mixed valency metal ions<sup>9,12,13</sup>, though under this class the earliest known classical compound is  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ . It is interesting to note that two high  $T_c$  molecular based ferromagnets are of this type—both mixed valence Cr(II)-Cr(III) cyanides—with magnetic ordering temperatures at 240 K and 90 K. Not many examples of homometal ions with differing spins are known to have ferromagnetic ordering.

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Compounds of considerable potential to be ferro or ferrimagnets can also be visualized by alternating homometal ions of similar valency but differing spins.  $\text{Fe}(\text{C}_5\text{H}_5)_2^+\text{FeBr}_4^-$  and  $\text{Fe}(\text{C}_5\text{H}_5)_2^+\text{FeI}_4^-$  are in this class although a greater stress in this paper is on the first compound. Synthetic methods and structures for these compounds have been reported earlier<sup>14</sup>. A structure proposed on the basis of detailed infrared spectral study by Sohar and Kuzsmann<sup>14</sup> has now been corroborated by the crystallographic study of Reiff *et al.*<sup>15,16</sup> and Evans *et al.*<sup>17</sup> The  $\text{Fe}(\text{C}_5\text{H}_5)_2^+\text{FeBr}_4^-$  has an orthorhombic layered structure with separate cation (with  $D_{5h}$  symmetry) and anion (tetrahedral) sublattices. The Mössbauer and magnetic properties of this compound<sup>15</sup> down to 4.5 K and another layered compound—a chloro analogue of the title compound—have already been documented<sup>16</sup>. The ferromagnetic state<sup>17</sup> shows no hysteresis which has been explained in terms of soft itinerant ferromagnetism; however, the exact nature of the magnetic ground states and the interaction between the two sublattices are open to questioning.

We report here a detailed spectroscopic study—EPR, Mössbauer (below 4.2 K) and infrared—on the bromo compound (which is found to have a  $T_c$  of 13.2 K) directed towards an understanding of the magnetic ground state. On the contrary, the iodo compound does not show any magnetic transition, but seems to have a low temperature structural phase transition.

## Materials and Methods

### Preparation

The preparation of ferricenium tetrabromo ferrate  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$  was done using a slightly modified literature procedure<sup>14</sup>. Ferrocene (Aldrich) (5 gm 0.026 mol) was dissolved in freshly distilled reagent grade carbon tetrachloride (10 ml). Similarly, liquid bromine (2.5 ml 0.015 mol) was dissolved in carbon tetrachloride (10 ml). The ferrocene solution was kept in ice cold water to avoid excessive heating. Bromine in  $\text{CCl}_4$  was added dropwise to the precooled ferrocene solution with constant stirring for one and a half hours. Finally the dark green precipitate formed was filtered and washed several times with carbon tetrachloride to remove any excess cyclopentadiene. The sample purity was checked by the presence of four intense bands in the IR spectrum<sup>14</sup> reported earlier and by elemental analysis (Found: C, 21.8; H, 1.83; Fe, 20.03; Br, 56.00%; Calc. for  $\text{C}_{10}\text{H}_{10}\text{Fe}_2\text{Br}_4$ : C, 21.35; H, 1.78; Fe, 19.93; Br, 56.94%). The

product was also characterized by X-ray powder diffraction (JCPDS, 23-1693). The isostructural iodo compound was prepared according to the literature procedure<sup>14</sup>. The elemental analysis shows the following data (Found: C, 16.3; H, 1.38; Fe, 15.03; I, 67.6%; Calc. for  $\text{C}_{10}\text{H}_{10}\text{Fe}_2\text{I}_4$ : C, 16.01; H, 1.33; Fe, 14.90; I, 67.74%).

### Physical measurements

**Infrared spectroscopy**—Vibrational spectrum of the pressed KBr pellet of the sample at room temperature was recorded on a Bruker model IFS 66v Fourier Transform IR spectrophotometer. Variable temperature infrared spectra were recorded with a Perkin-Elmer PE983 IR spectrophotometer. The resolution at which the spectra were recorded, was  $2\text{ cm}^{-1}$ . A Leybold closed cycle helium cryostat was used for the measurements. The samples were mounted in the form of pressed KBr pellets on a KBr window for the variable temperature measurements.

**Magnetic measurements**—Magnetic properties were investigated using a Quantum Design SQUID magnetometer in the temperature range of 400-2 K at Morris Research Inc, Berkeley. The sample in the form of a pressed pellet was mounted on the sample probe of the magnetometer made of a thin polyethylene tube using a teflon tape. An investigation of the polycrystalline powder showed that pressing did not have any effect on magnetism. A series of blank measurements were made to determine the magnitude of the magnetization ( $M$ , emu/g) and the dependence of magnetization on temperature and applied field. The blank showed five orders of magnitude smaller values than the sample, consequently no corrections were made for the sample holder. The blank was diamagnetic throughout the temperature range of 2 to 400 K. The diamagnetic correction for the compound was found to be  $-172.7 \times 10^{-6}$  c.g.s. e.m.u.

**EPR spectroscopy**—The EPR measurements were made with both the Varian E-112 EPR instrument as well as the IBM ER-200D SRC spectrometer, both operating at X band frequencies with a 100 kHz modulation. Low temperature measurements were made in the Varian equipment using an Oxford ESR 900 continuous flow cryostat, while the ER-200D instrument was attached to a liquid transfer Helitran cryogenic unit (model LTD-3-110, Air Products and Chemicals, Inc., Allentown, PA) in conjunction with an APD-E temperature controller used to regulate the sample temperature in the EPR cavity down to 6 K. In

both cases, liquid helium was used as the cryogen. Measurements on the ER-200D EPR instrument also used an IBM computer for data collection and retrieval with a computer program written by Dr. A. Levy. Microwave frequency was calibrated with DPPH g-marker.

**Mössbauer spectroscopy**—Initial Mössbauer measurements were made in the Canberra S-100 Mössbauer spectrometer with a Wissel constant acceleration drive down to 77 K. The source was Co/(Pd), (Amersham, 50 mCi). Lower temperature measurements were done in another instrument<sup>18</sup> where a constant acceleration type Mössbauer spectrometer together with a 1024-channel analyzer operating in the time scale mode were employed. The source Co/Rh (25 mCi, Amersham) was kept at room temperature for all measurements. Velocity calibration was performed with the known hyperfine splitting in the spectrum of metallic iron, and the isomer shifts reported here are relative to  $\alpha$ -Fe at room temperature. The low temperature spectra were collected by means of a helium bath cryostat. The Mössbauer spectra were analyzed using a computer program (MOSFUN) using Lorentzian line shapes.

**Differential scanning calorimetry**—Differential scanning calorimetry measurements were done in a Version V. 5.40 instrument in the range of 113 to 273 K. 2.88 mg of tetrabromoferrate and 3.38 mg of tetraiodoferrate were used for the measurements

## Results and Discussion

Evans *et al.*<sup>17</sup> described the crystal structure of the title compound to be of orthorhombic in nature with space group of Pmcn and  $a = 9.036(3)$   $b = 12.137(2)$ ,  $c = 14.192(2)$  Å. The  $[\text{FeBr}_4]^-$  units are perfectly tetrahedral and the ferricenium ions have a  $D_{5h}$  symmetry with eclipsed cyclopentadienyl rings. Reiff *et al.*<sup>15</sup> reported that the molecules have an orthorhombic layered structure with a space group of Pmna. These two space groups are not transformable from one another. Thus, there seems to be a controversy in the space group of the material. Structure based purely on a detailed analysis of infrared spectra has the following features: 1) The cyclopentadienyl anion is said to have  $D_{5h}$  symmetry in conformity with the presence of four infrared bands in the region of 4000 to 500  $\text{cm}^{-1}$  and there is no coupling between vibrations of the cyclopentadienyl rings (note that a  $D_{5d}$  structure should have given rise to 10 bands). 2) The  $[\text{FeBr}_4]^-$  moiety has a tetrahedral disposition. These interpretations based on infrared

spectral data are in good agreement with the molecular structural details reported later by two independent groups<sup>15,17</sup>. The structural features also indicate that there is considerable interaction between the cyclopentadienyl rings and the bromine atoms of  $[\text{FeBr}_4]^-$ . Consequently the  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$  cation will have a low spin  $d^5$ , ( $a_{1g}^2 e_{2g}^3$ ) electronic configuration resulting in a  ${}^2E_{2g}$  ground state in the  $D_{5h}$  point group while the  $\text{FeBr}_4^-$  anion will have a high spin  $d^5$  ( $e_g^2 t_2g^3$ ) electronic configuration, possessing a  ${}^6A_1$  ground state in the  $T_d$  symmetry. Hence the  $D^+A^-$  system is a combination of a low spin  $d^5$  and a high spin  $d^5$  configuration arising from a possible one dimensional chain of homometal ions of same valency but differing spin values.

## Magnetism

Though the emphasis in this work is on the bromo lattice in view of the earlier reports on its structural and magnetic properties, a comparison with its iodo analogue brings out some interesting correlations. Our magnetic measurements on the iodo lattice shown in Fig. 1(a) reveal that the magnetic moment values were constant until about 50 K at  $3.36 \mu_B$ . Below 50 K, the magnetic moment decreases sharply and reaches a minimum value of  $2.7 \mu_B$  at 2 K. The plot of  $1/\chi$  vs.  $T$  shows a straight line with no considerable change at low temperature. The entire temperature region for this iodo compound could be fitted for simple Curie-Weiss law with a  $\theta$  value of -5 K. On the other hand the magnetism of the bromo lattice above 20 K can be explained in terms of a Curie-Weiss law and the linear variation of  $\chi^{-1}$  with  $T$  brings out a value for the Weiss constant  $\theta = -23\text{K}$ , indicating the spin centers to be antiferromagnetically coupled with a ferrimagnetic ordering. Below 15 K, however,  $\chi^{-1}$  decreases sharply indicating a long range ferromagnetic transition. However, the absence of a positive  $\theta$  greater than  $T_c$  is, though rare, possible for an itinerant ferromagnet<sup>19,20</sup>. The magnetic measurement down to nearly 5 K by Reiff *et al.*<sup>15</sup> are in total agreement with our measurement. The ferromagnetic transition is also manifested in the magnetization measurements. Fig. 1(b) shows the magnetization data of the sample at two different applied fields, 1 Oe and 100 Oe. Below 13.2 K the magnetization increases sharply indicating the ferromagnetic character of the long range spin correlation. The long range correlation which we interpret is actually supported by the measurements of Reiff *et al.*<sup>15</sup> by a sharp decrease of  $\chi_m^{-1}$  below 2.47 K.

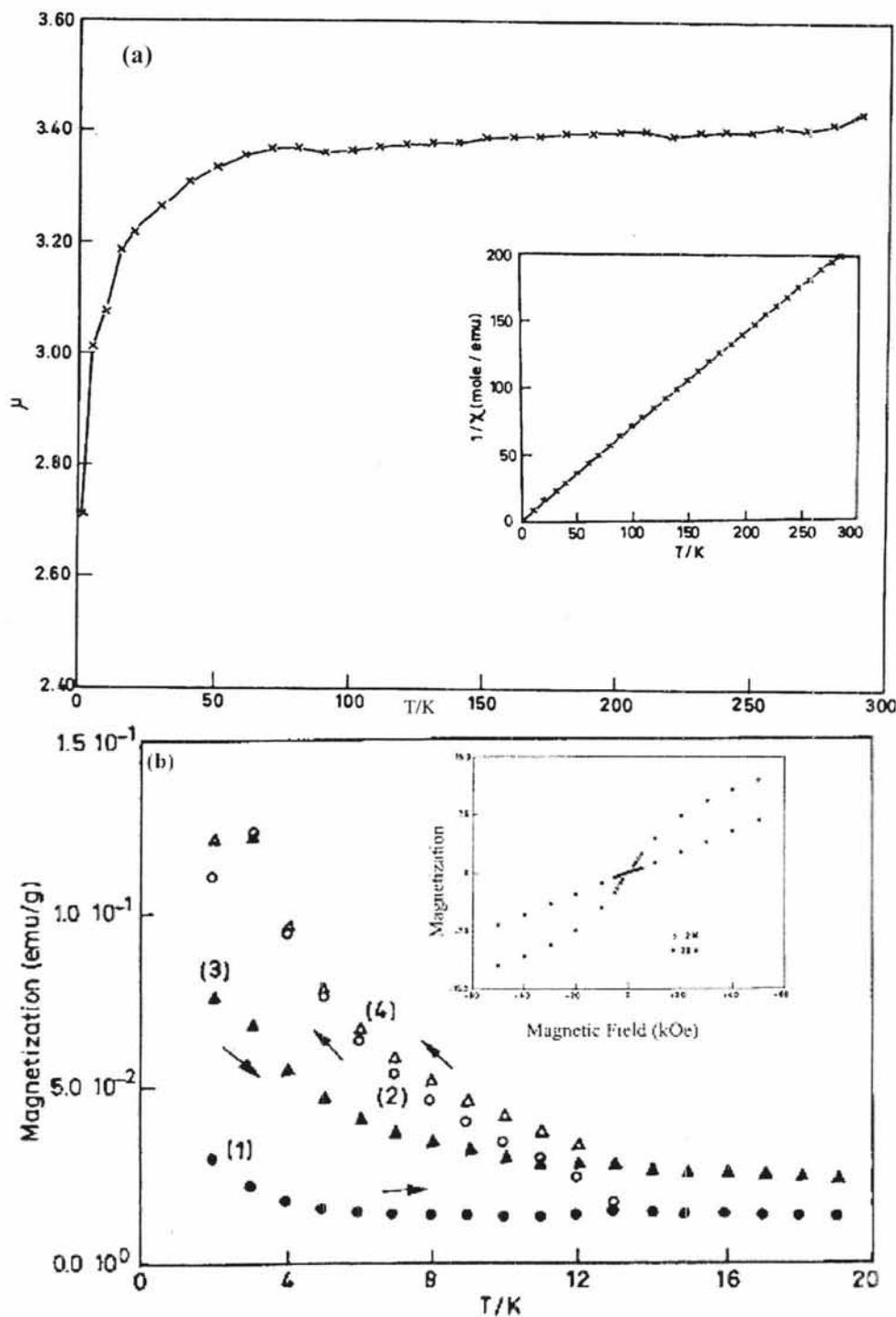


Fig. 1(a)—Plot of temperature dependent magnetic moment for  $C_{10}H_{10}Fe_2I_4$ . Inset shows the temperature dependent inverse magnetic susceptibility ( $\chi^{-1}$ ) for  $C_{10}H_{10}Fe_2I_4$ ; (b)—The magnetization of the sample  $[Fe(C_5H_5)_2]^+ [FeBr_4]^-$  measured at two different applied fields 1 and 100 Oe near the transition temperature. The sample was cooled in zero field and measurements were done during warm-up ( $\bullet$ ) in an applied field of 1 Oe (curve 1). After reaching 20 K, the sample was cooled ( $\circ$ ) in 10e (curve 2). In a second procedure the sample was cooled in zero field and the field was turned on to 100 Oe at a sample temperature of 2 K and the above procedure was repeated (curves 3 ( $\blacktriangle$ ) and 4 ( $\triangle$ )). The data clearly indicates a ferromagnetic transition at 13.2 K. Large difference in magnetization is seen between cooling and warming. The 1 Oe data have been multiplied by 7 to make the ordinate comparable to the 100 Oe data. In the 1 Oe data, magnetization above 13.2 K is about  $3 \times 10^{-5} \text{ emu g}^{-1}$ . Inset denotes the magnetization versus applied field at two different temperatures 2K ( $\circ$ ) and 20K ( $\bullet$ ). Below 13.2 K the  $M$  versus  $H$  curve shows the characteristic ferromagnetic "S" shape, above which the magnetization varies linearly with the applied field. No correction has been made for the sample holder.

A magnetization of  $0.12 \text{ emu g}^{-1}$  corresponds to an effective magnetic moment of  $0.1\mu$  per formula unit of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$ . The difference between cooling and warming indicates the presence of a hysteresis and the effect of hysteresis is much larger at lower applied fields.

The transition temperature, defined as the intersection of the linear extrapolation of the magnetization curve from the high and low temperature regions did not show a strong field dependence. However, magnetization below  $T_c$  showed strong field dependence. The plots of  $M$  versus  $H$  for 2 K and 20 K shown as an inset in Fig. 1(b) reveal a characteristic ferromagnetic "S" shape in the low temperature measurement. For temperatures ( $>20 \text{ K}$ ) above  $T_c$ , the plot is linear. Saturation occurs above 5 T.

The positive indication for  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$  being a ferromagnet comes from the sharp rise in magnetization even at an applied field of 1 Oe, the presence of temperature hysteresis and "S" shaped curve in  $M$  versus  $H$  below  $T_c$ . Within experimental uncertainty, no hysteresis or coercivity was observed and hence the material can be a soft ferromagnet. The magnetic data presented here might alternatively be interpreted as superparamagnetism, ferrimagnetism, or field induced ferromagnetism. However, these possibilities cannot completely explain the data. In superparamagnetism the magnetization below  $T_c$  should scale<sup>15</sup> as  $H/T$  and this was not observed (see also the discussion under Mössbauer spectroscopy). In ferrimagnetism, the temperature dependent difference in sublattice magnetizations would make  $M$  to decrease below a certain temperature and again this was not observed. The isothermal  $M$  vs  $H$  plot does not show any field induced transition which would result from a field induced ferromagnetism. It looks that the cationic sublattice orders at a much lower temperature than the anionic sublattice. Hence at sufficiently low temperatures, long range 3D order has occurred through weak inter-layer interactions.

The difference in the magnetic behaviour of the iodo compound compared to that of the bromo derivative could be due to the large spin-orbit coupling of iodine, which prevents the molecule from 3-dimensional ordering.

#### EPR spectroscopy

The temperature dependent EPR spectra of a polycrystalline sample of the title compound is shown in Fig. 2 for the region of 300 to 7.7 K. Down to

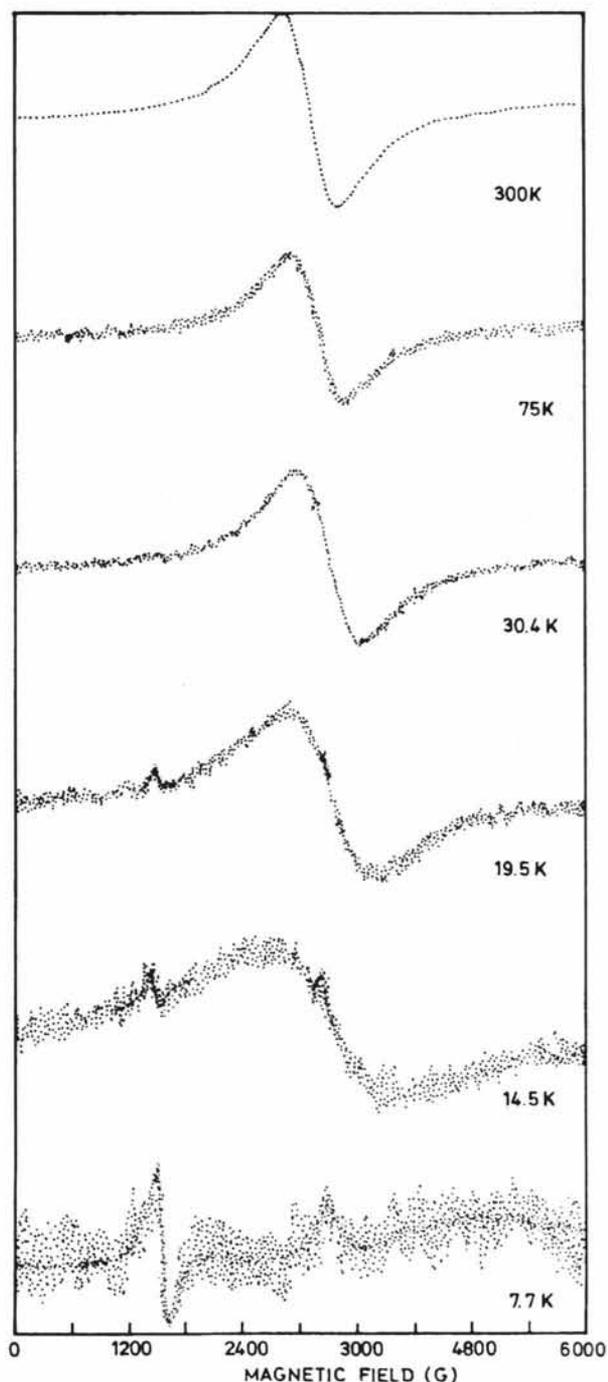


Fig. 2—Temperature dependent (7.7-300 K) EPR spectra of polycrystalline sample of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$  at X-band frequency with 100 kHz modulation.

50 K, the spectrum is composed of a single "isotropic looking" line at  $g = 1.885$ , with a peak to peak line width,  $\Delta H$  of approximately 55 mT. The line width remains almost constant down to nearly 50 K; on further lowering of temperature, the line gets further broadened. At 19.5 K two remarkable features are

noted: (i) the line at  $g = 1.885$  tends to become much broader indicating a loss of signal on further cooling; and (ii) two new lines appear at  $g_{\parallel} = 4.09$  and  $g_{\perp} = 1.995$ .

At 14.5 K where there was a magnetic transition as noted by the susceptibility measurements (*vide supra*), the original isotropic line almost disappears due to infinite broadening leaving only the lines of low intensities at  $g = 4.09$  and 1.995-related respectively, to the  $g_{\parallel}$  and  $g_{\perp}$  components of the ferricenium ion<sup>21-25</sup>. Further cooling of the sample reveals the presence of only these two latter lines with a trace of intensity of the isotropic line which tends to broaden and hence distort the  $g_{\perp} = 1.995$  line.

The isotropic line at  $g = 1.885$  is due to  $\text{FeBr}_4^-$  ion in its  ${}^6\text{A}_1$  ground state. The slight departure from the free electron value should not only be due to covalency but also due to configurational mixing with the excited state wave functions, inclusive of spin-orbit effect from bromine. Below 14 K, the establishment of a canted antiferromagnetic interaction in the lattice of  $\text{FeBr}_4^-$  ion, as suggested by Reiff *et al.*<sup>16</sup>, must be responsible for the total broadening of this EPR signal at  $g = 1.885$ . The  ${}^2E_g$  or  ${}^2E$  ground state, depending on the  $D_{5h}$  or slightly reduced symmetry allows for rapid spin-lattice relaxation and highly anisotropic  $g$  tensor as derived from expressions for  $g$  values appropriate for the cation<sup>22</sup>.

$$g_{\parallel} = 2 + 4k_{\parallel} [-(\xi/\delta)/(1+(\xi^2/\delta^2)^{1/2})] \quad \dots (1)$$

$$g_{\perp} = 2/(1+(\xi^2/\delta^2)^{1/2}) \quad \dots (2)$$

where  $k$ ,  $\xi$ ,  $\delta$  represent, respectively the orbital reduction factor, spin-orbit coupling for  $\text{Fe}^{3+}$  and one electron orbital energy splitting due to distortion from  $D_5$  symmetry<sup>21-24</sup>. The literature values<sup>21-25</sup> of  $g_{\parallel}$  vary from 3.83 to 4.43 and  $g_{\perp}$  from 1.26 to 1.92 for ferricenium cation. Our values of  $g_{\parallel} = 4.09$  and  $g_{\perp} = 1.995$  are close to those in  $[\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2]^+\text{PF}_6^-$ . Furthermore, a  $\Delta g$  of  $(4.09 - 1.995) = 2.095$  is among the lowest reported thus far, again in similarity to  $[\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2]^+\text{PF}_6^-$ . Such a lower  $\Delta g$  value is inherently a reflection of the  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$  part having a lower symmetry than rigorous  $D_{5h}$ .

Generally, the EPR spectrum of the ferricenium cation is only observable in dilute conditions at around liquid helium temperature. The broadening and subsequent loss of EPR line at  $g = 1.885$  and the

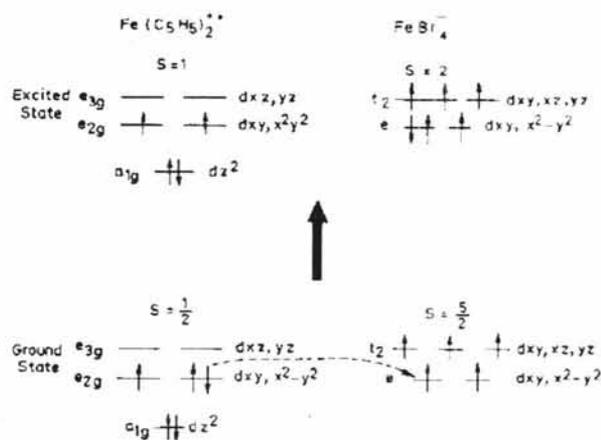


Fig. 3—Schematic ground and excited state electronic structures of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$ . The orbital notation for  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$  is that of original  $D_{5h}$  symmetry but this structure could be reduced to  $D_5$  or lower symmetry in the compound.

emergence of lines at  $g = 4.09$  and 1.995 indicate the formation of a domain of the  $D^+A^-$  complex. It could even be safely concluded that the complex after near-neighbour ferrimagnetic interaction tends to have a configurational mixing with  $a_{1g}^2 e_{2g}^2$  ( $D^+$ ) (or  $a_1^2 e_2^2$  for reduced symmetry) ( $e$ )<sup>3</sup> ( $t_2$ )<sup>3</sup> ( $A^-$ ), a  $d^4-d^6$  type electronic configuration, more probably a  $d^4 \uparrow \downarrow d^4$  situation, on a donor-acceptor site; the first  $d^4$  having a paired and two unpaired ( $S=1$ ) electrons while the second  $d^4$  has four unpaired electrons (Fig. 3). Such a situation may lead to rapid spin-lattice relaxation manifested by the disappearance of the first line and also the formation of the other two at low temperatures. However, another suitable mechanism would be the creation of a larger dipolar field from the ferricenium part because of addition of one more unpaired electron to this site as a result of charge-transfer which in turn would broaden the isotropic EPR line due to  $\text{FeBr}_4^-$ . This is more plausible when seen in the context of Mössbauer spectroscopy (*vide infra*). This is also in tune with the prediction of near-neighbour ferrimagnetic coupling in  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$ . What is remarkable is the total disappearance of the line at  $g = 1.885$  from 13 K downwards—a magnetic transition point, in complete agreement with the susceptibility experiment.

We have attempted to plot the  $\Delta H$  for  $g = 1.885$  line as a function of temperature (Fig. 4). The plot reveals that the line width remains practically constant until about 30 K in conformity with the Curie-Weiss plot for susceptibility. At the same time, around 20 K the  $\Delta H$  begins to rise up sharply, while at approximately 13 K the line is infinitely broadened

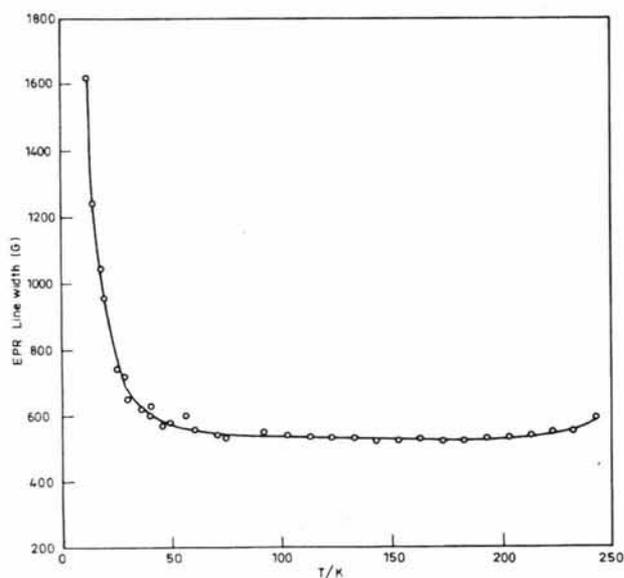


Fig. 4—Plot of line width ( $\Delta H$ ) of  $g = 1.885$  EPR line corresponding to  $\text{FeBr}_4^-$  as a function of temperature.

again showing the complementary nature of the results from susceptibility and EPR measurements. Both our EPR work and the magnetic and Mossbauer results of Reiff *et al.*<sup>15</sup> agree on the transition temperature.

In order to understand the molecular structure in solution and to see the effect of bringing the material into solution, we have measured the EPR of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$  in dry methanol at 77 K, since no spectrum could be observed at room temperature. The total EPR spectrum is a combination of those due to two species: (a)  $\text{Fe}(\text{C}_5\text{H}_5)_2^+$  part as its  $g$  values ( $g_{\parallel} = 4.14$  and  $g_{\perp} = 1.99$ ) are comparable to those measured earlier<sup>23</sup> and (b) a methanol coordinated  $\text{FeBr}_4(\text{MeOH})_2^-$  with  $g_{\perp} = 6.1$  and  $g_{\parallel} = 2.0$  expected for a tetragonally distorted octahedral high spin  $\text{Fe}^{\text{III}}$  center with a large  $\Delta$  value. This proves not only the presence of the two ions but also the differences in the solid state and solution properties. The fact that the ferricenium resonance in solid is measurable only below 20 K in contrast to the free ferricenium cation observed in solution even at 77 K, is a good indication of the existence of exchange interaction between the  $\text{D}^+$  and  $\text{A}^-$  species in the solid state.

No EPR spectrum was observed for the iodo compound down to 77 K in both solid and solution states.

#### Mössbauer spectroscopy

Quite a few ferricenium cation containing materials have been studied by Mössbauer spectroscopy,

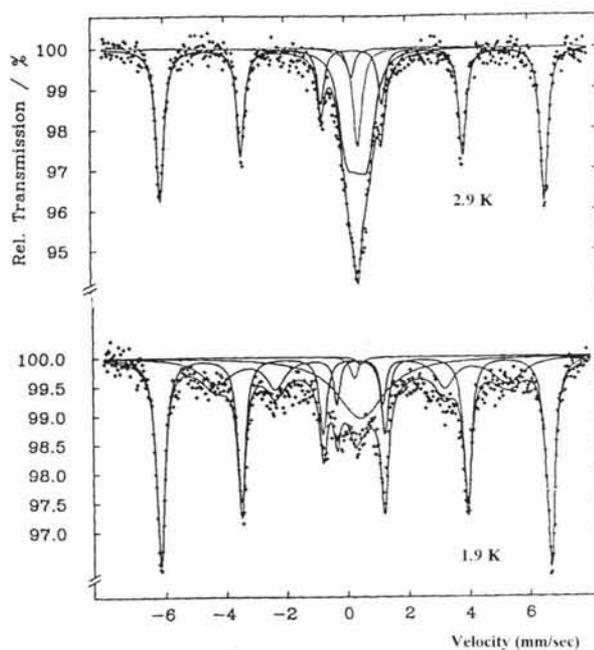


Fig. 5— $^{57}\text{Fe}$  Mössbauer spectra of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$  at the lowest two different temperatures 2.9 K and 1.7 K, in zero applied field.

especially the ones containing the decamethyl ferricenium ion. The counter ions used were either paramagnetic or diamagnetic<sup>3-7,25-28</sup>. The paramagnetic anions have been mostly  $\text{TCNE}^-$ ,  $\text{TCNQ}^-$ ,  $\text{DDQ}^-$  and even some metal dithiolenes. Such radical ions may provide an internal dipolar field leading to slow paramagnetic relaxation and hence broadening of the peak. Temperature dependent Mössbauer spectra of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$  down to 4.5 K have already been reported by Reiff *et al.*<sup>15</sup>. Our data measured down to 1.7 K are not only in full agreement with this earlier work down to 4.7 K but also gives additional information, especially at 1.7 K. The spectral data at 2.9 and 1.7 K alone are shown in Fig. 5. The ambient temperature  $^{57}\text{Fe}$  Mössbauer spectrum of this compound exhibits a slightly broadened line resolvable into two absorption lines of almost similar intensities corresponding to the two centers with an individual line-width of 0.30 mm/sec to 0.36 mm/sec with no observable quadrupole resolution. This situation continues down to 15 K but a broad peak with indications of resolution into a sextet shows up at 14 K. Appearance of a clear six line pattern from one of the centers (due to the slow relaxing magnetic hyperfine component) occurs at 13 K in good coincidence with the inflection point at 13.2 K in the susceptibility experiments and the disappearance of the  $g = 1.885$  EPR line at 13 K—a temperature of

great importance in terms of electronic relaxation due to the  $\text{FeBr}_4^-$  component of the compound. The  $T_c$  is thus confirmed at 13 K from all three measurements. Further cooling down to 2.9 K results in the broadening of the second singlet line which also ultimately resolves into another sextet at 1.7 K.

The compound  $[\text{NEt}_4][\text{FeBr}_4]$  containing a tetrahedrally structured  $\text{FeBr}_4^-$  has been found to give a chemical shift of 0.36 mm/sec<sup>29,30</sup>. The chemical isomer shift of one of the species of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$  is in the range of 0.32 mm/sec to 0.35 mm/sec over the studied temperature region. As mentioned before, configurational mixing with the excited state  $a_{1g}^2 e_{2g}^2 (D^+) (e)^3 (t_2)^3 (A^-)$  with charge transfer from  $D^+$  to  $A^-$  must be responsible for producing a large dipolar field at the  $\text{FeBr}_4^-$  site leading to slow paramagnetic relaxation at this site, a necessary condition for the spectral resolution of a Mössbauer sextet. Furthermore, the same charge—transfer and/or the canted antiferromagnetic ordering explains the disappearance of the EPR signal due to  $\text{FeBr}_4^-$ . The internal magnetic field of this component works out to 400 kG at 1.7 K, close to the value of  $[\text{NEt}_4][\text{FeBr}_4]$ , which is 420 kG. All of these together suggest that the first species undergoing magnetic ordering is  $[\text{FeBr}_4]^-$ . Only one component of this salt, namely the  $\text{FeBr}_4^-$  exhibits cooperative long range ordering below 13.2 K as seen from the spontaneous magnetic hyperfine splitting in zero applied field. Our data at 2.9 K and 1.7 K further proves the long range ordering of the cationic lattice as well which is evidenced by the appearance of a second magnetic hyperfine splitting in zero field — due to the ferricenium cation. It is no doubt now that both sublattices, having been ordered, lead to the total 3D ordering and hence the formation of ferromagnetic domains at and below 2.7 K.

On the other hand, the chemical isomer shift value of 0.56 mm/sec for species II in the present compound is close to the values of  $> 0.42$  mm/sec reported for most ferricenium compounds<sup>3-7,25-28</sup> which allows us to identify the second component to originate from the ferricenium cation. However, its saturation  $H_n$  value of 326 kG is much smaller than that reported for ferricenium compounds.

Another important point to note here is that the internal hyperfine field ( $H_n$ ) on both centers is temperature dependent as can be seen in Fig. 6. This temperature dependence of  $H_n$  clearly indicates that the relaxation processes controlling the Mössbauer

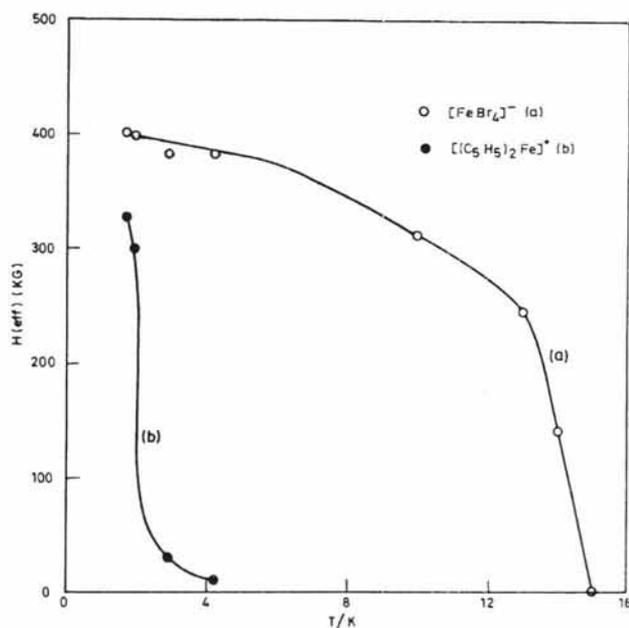


Fig. 6—Temperature dependence of internal magnetic field in Mössbauer centres I and II of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+[\text{FeBr}_4]^-$ . (a)  $\text{FeBr}_4^-$  ( $\circ$ ) and (b)  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$  ( $\bullet$ ).

spectrum are not of superparamagnetic origin in accordance with our susceptibility results. Also this temperature dependence is attributed to slow paramagnetic (spin-orbit) relaxation broadening and 3D ferromagnetic ordering. However, the other ferricenium salts that have so far been reported in the literature show a constant internal magnetic field throughout the slow relaxation regime as indicated by the fixed spectral positions of the six Mössbauer spectral lines<sup>31</sup>. Mössbauer line broadening at 14 K and the line broadening of the  $g = 1.885$  EPR line from the  $\text{FeBr}_4^-$  component around the same temperature not only indicate the origin of the centers responsible for these effects but also suggest a possible co-operative effect likely to be similar to a soliton involvement<sup>32</sup>. However, a somewhat sudden appearance of Zeeman splitting for both centers, large values for  $dH_n/dT$  and their coincidence with the temperature dependent susceptibility and EPR data collectively indicate a three dimensional ordering, in this case a ferromagnetic one.

A value for  $H_n$  of 400 kG for  $\text{FeBr}_4^-$  in this compound is slightly less than that in  $\text{NEt}_4\text{FeBr}_4$ . On the other hand, a much reduced value of 326 kG was measured for the ferricenium part of the compound. Other similar ferricenium salts with radical anions as counter ions usually have an internal field of 400 kG. The most possible mechanism for ferromagnetic spin

coupling could be based on spin polarization<sup>33</sup> which was used for explaining such properties of some metallocenium CT salts by Kahn and co-workers<sup>34,35</sup>.

Variable temperature Mössbauer spectra were recorded for  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+ [\text{FeI}_4]^-$  as well in the temperature range of 300 to 1.7 K (Fig. 7). It is very interesting to note that no magnetic hyperfine split lines appear even at 1.7 K. But there are indications of broadening of both the components in the spectra. Most probably this broadening is due to fast relaxation as a result of strong spin-orbit coupling. The reduction of  $H_{\text{eff}}$  may be due to an orbital magnetic field contribution with opposite sign to that arising from the Fe spin of 5/2 and core polarization.

#### *Differential scanning calorimetry and infrared spectroscopy*

In order to understand the magnetic ordering in more detail, we thought it instructive to perform variable temperature infrared measurements on these systems. It may be noted that ferrocene itself shows a structural phase transition (a  $\lambda$  transition) at around 164 K<sup>36</sup>. The low temperature phase was shown to be one in which ferrocene is in  $D_{5d}$  symmetry. This transition has been confirmed by Rocquet *et al.*<sup>37</sup> who performed IR measurements in the range of 4000 to 20  $\text{cm}^{-1}$  down to 13 K.  $\text{FeBr}_4^-$  ion is shown to be of  $T_d$  symmetry using combined IR and Mössbauer measurements<sup>30</sup>. However, no low temperature infrared data are available to the best of our knowledge in the literature on  $\text{FeBr}_4^-$  ion.

We have performed differential scanning calorimetric (DSC) measurements on the complex to ascertain whether there is indeed a phase transition. The DSC data show structural transitions at 124 K and 258 K. The transition at 124 K has a  $\Delta H$  of 17.36  $\text{kJ mol}^{-1}$  and  $\Delta S$  of 140  $\text{J K}^{-1}\text{mol}^{-1}$  higher than the values of the ferrocene phase transition at 164 K<sup>38</sup>. The occurrence of the transition at 124 K and the similarities in the variable temperature infrared spectra (see below) between the two compounds suggest that the transition is indeed similar to that of ferrocene. The decrease in temperature for the phase transition could be correlated with the electron transfer from the ferricenium part resulting in a weakening of the metal-ring bond. This will result in a lesser energy barrier for the rotation of the cyclopentadienyl rings which in turn occurs at a lower temperature than ferrocene. The 258 K transition can be similarly correlated to the metastable phase of ferrocene as observed earlier<sup>38</sup>.

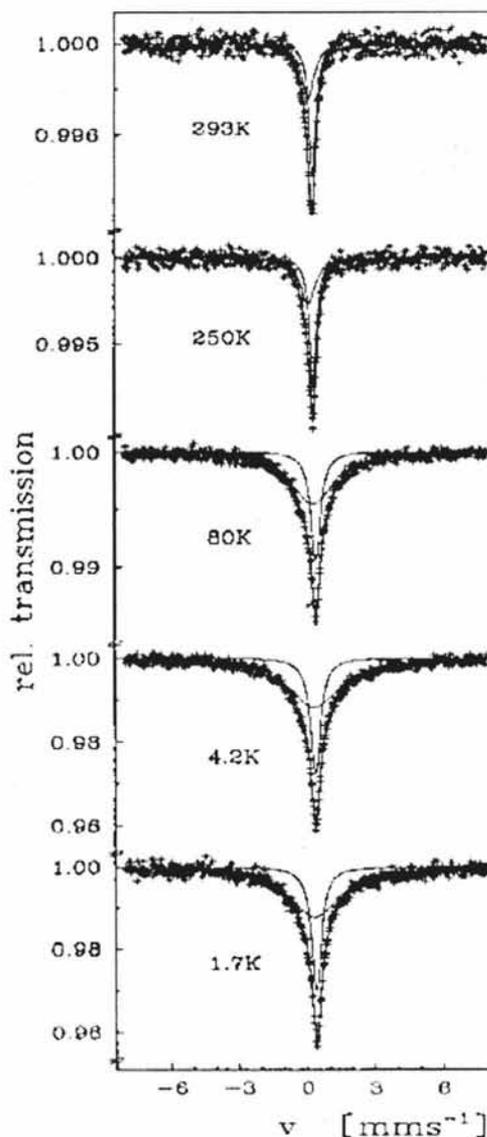


Fig. 7—Variable temperature  $^{57}\text{Fe}$  Mössbauer spectra of  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+ [\text{FeI}_4]^-$  in zero applied field.

The variable temperature IR spectra of the complex in the temperature range of 76 K to room temperature from 600 to 1500  $\text{cm}^{-1}$  are shown in Fig. 8a. The band at 855  $\text{cm}^{-1}$  is assigned to C-H perpendicular bend which shows negligible change along the phase transition. This behaviour is parallel to that observed in ferrocene. The broad band at 1010  $\text{cm}^{-1}$  however, (Fig. 8a) shows greater changes. At 200 K, the peak begins to split into two and upon further cooling to 130 K, a clear three peak structure is resolved. This observed splitting could be compared with that of ferrocene in which the two bands of 1:2 intensity are resolved around the structural transition. The symmetric C-C stretching region in ferrocene shows

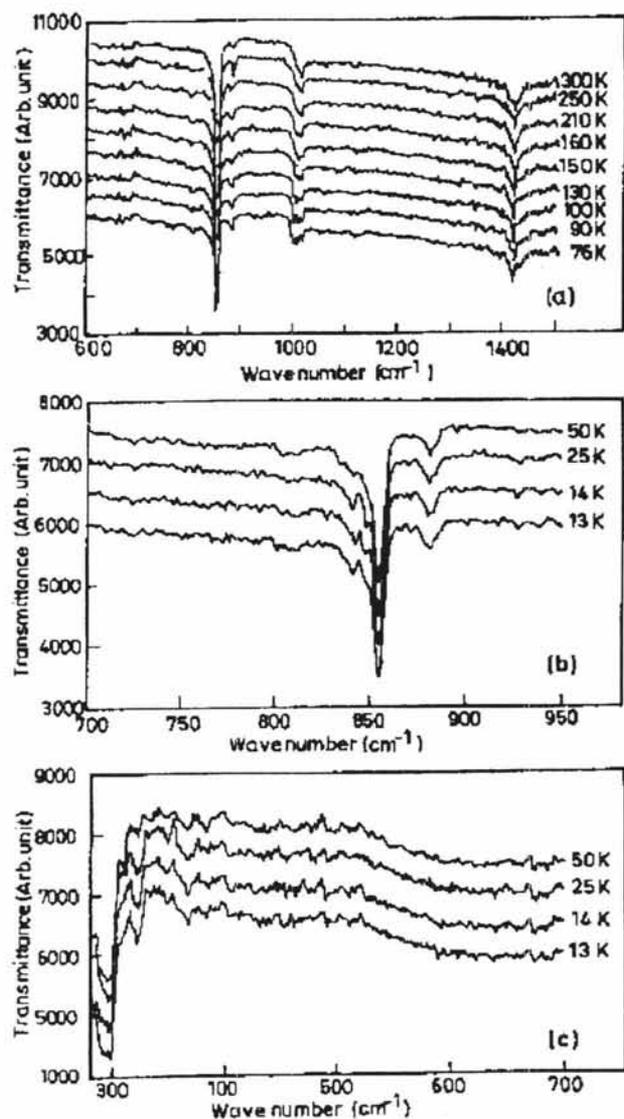


Fig. 8—(a) IR spectrum of  $C_{10}H_{10}Fe_2Br_4$  from 76 K to 300 K in the range of  $600\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$  IR spectra of the  $C_{10}H_{10}Fe_2Br_4$  during the magnetic transition; (b)  $700$  to  $950\text{ cm}^{-1}$ ; (c)  $280$  to  $700\text{ cm}^{-1}$ . (b and c in the region 50–13 K).

significant intensity changes upon phase transition. The effect is not so pronounced in ferricenium tetrabromoferrate, but is clearly visible below 100 K (Fig. 8a). The structural transition at 258 K is not manifested in the infrared spectrum; this behaviour is consistent with ferrocene itself<sup>37</sup>.

The spectrum at 25 K in the range of  $750$  to  $900\text{ cm}^{-1}$  shows the emergence of side bands on  $\nu(\text{CH})$  bend which is further more pronounced at 14 K (Fig. 8b). This is the temperature range at which we see marked changes in the EPR, Mössbauer and magnetic measurements. In Fig. 8c we show infrared spectra in the  $280$  to  $700\text{ cm}^{-1}$  range for the same

temperatures. The emergence of a new peak at  $312\text{ cm}^{-1}$  is clearly visible. The point to be emphasized is that the spectra at all other regions remain exactly the same and new structures are confined only to certain specific vibrations which are most affected by magnetic ordering. As may be recalled from the earlier discussion on magnetic ordering, we propose an electron transfer from the ferricenium part to the tetrabromoferrate part as the reason for the change in magnetization at 14 K. This electron transfer could lead to an increase in the electron density in the Fe-Br bonds, since the electron transfer is to the  $e_g(d_{x^2-y^2})$  orbital. This change in the electronic structure manifests itself in the form of two important effects in the IR spectra: a) An emergence of features at  $830\text{ cm}^{-1}$  and  $845\text{ cm}^{-1}$  adjacent to the  $\nu_{19}\gamma(\text{CH}) E_{1u}$  mode attributed to the perpendicular C-H bending mode, which is red-shifted due to electron transfer, and, b) A new feature adjacent to the  $\nu$  Fe-Br stretching at  $310\text{ cm}^{-1}$  due to strengthening of the Fe-Br bond. However, there may also be additional features in the  $\nu_{32}(E_{2u}\text{ C}=\text{C})$  region around  $1425\text{ cm}^{-1}$ . Low intensity of this feature makes us defer any conclusive statement.

To understand the nature of the magnetic ordering in tetrabromoferrate and to correlate the structure of this compound with that of the tetraiodoferrate, we performed variable temperature infrared measurements on ferricenium tetraiodoferrate as well. Note that differential scanning calorimetry measurements show two distinct transitions at 126 K and 252 K for the iodo compound, which are similar to that of the tetrabromoferrate having similar values for the  $\Delta H$  and  $\Delta S$  (At 126 K,  $\Delta H = 11.04\text{ kJ mol}^{-1}$  and  $\Delta S = 87\text{ J K}^{-1}\text{ mol}^{-1}$  and at 252 K,  $\Delta H = 63\text{ kJ mol}^{-1}$  and  $\Delta S = 250\text{ J K}^{-1}\text{ mol}^{-1}$ ). Variable temperature infrared spectra from 200 to 15 K are shown in Fig. 9a. In the 100 to 300 K range, we expect changes in the infrared spectral patterns due to phase transitions at 126 and 252 K, although the 252 K transition is not clearly visible in the IR spectra as shown in the case of tetrabromoferrate. In the low temperature range from 201 to 15 K (Figs 9a and 9b), we see emergence of new bands in the IR spectra which are totally absent in the high temperature range. The bands which appear are at  $1262\text{ cm}^{-1}$ ,  $943\text{ cm}^{-1}$ ,  $821\text{ cm}^{-1}$  and  $430\text{ cm}^{-1}$ . This could be explained on the basis of another structural transition below 100 K, but we could not perform differential scanning calorimetry (DSC) in this temperature range to confirm a phase transition. The drastic difference in

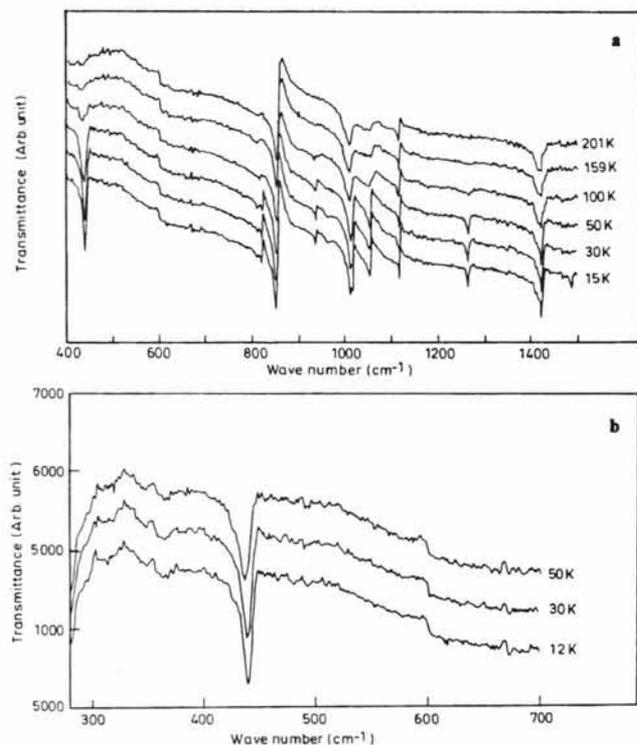


Fig. 9—(a) Variable temperature IR spectra of  $C_{10}H_{10}Fe_2I_4$  in the region of 300-15K. Note the emergence of the new peaks below 100 K. (b) Infrared spectra from 50 K to 12 K in the range of  $280\text{ cm}^{-1}$  to  $700\text{ cm}^{-1}$ . Note that no additional peaks are apparent in this temperature range.

the spectra of the tetraiodoferrate from the tetrabromoferrate and ferrocene below 100 K can be explained by suggesting that it is this low temperature phase transition which prevents the molecule from undergoing magnetic ordering. Although the phase transition at 126 K is manifested in the infrared just as in tetrabromoferrate, no changes are seen in the low temperature spectra (Fig. 9b). Concomitantly, no changes are seen in the magnetic, EPR and Mössbauer measurements.

### Conclusion

A combined look at the results of all four measurements gives a consistent picture of a near-neighbour antiferromagnetic coupling in  $[Fe(C_5H_5)_2]^+ [FeBr_4]^-$  leading to a ferrimagnetic state with a  $T_c$  of 13 K and a three dimensional ferromagnetic ordering below 4 K. IR and DSC measurements suggest a distinct low temperature phase for the compound<sup>39</sup>. Magnetic ordering results in the emergence of new bands in the IR spectrum. A schematic illustration of the electronic structure to understand the near neighbour exchange interaction is presented in Fig. 3.

Although we have assumed a  $D_{5h}$  symmetry, a structural distortion leading to a lower point group symmetry would also result in the same final state as far as the spin is concerned. However, given the pseudo-one dimensional nature of the interaction, electronic transition leading to magnetic ordering is not altogether unexpected. The electronic relaxation properties, EPR and the Mössbauer properties are explainable by a spin polarization mechanism involving configurational mixing due to  $D^+ \rightarrow A^-$  charge transfer. However in the case of  $[Fe(C_5H_5)_2]^+ [FeI_4]^-$ , presence of a low temperature phase below 100 K prevents magnetic ordering in  $C_{10}H_{10}Fe_2I_4$  although additional aspects such as the large spin-orbit coupling also need to be considered to explain the magnetism better.

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