

Synthesis and characterization of novel charge transfer complexes formed by *N,N'*-bis(ferrocenylmethylidene)-*p*-phenylenediamine and *N*-(ferrocenylmethylidene)aniline

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Abstract

N,N'-Bis(ferrocenylmethylidene)-*p*-phenylenediamine **1** and *N*-(ferrocenylmethylidene) aniline **2** are readily synthesized by Schiff base condensation of appropriate units. Iodine (I₂), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachloro-1,4-benzoquinone (CA), tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) form charge transfer complexes with **1** and **2**. IR spectroscopy suggests an increase in the amount of charge transferred from the ferrocenyl ring to the oxidant in the order, I₂ < CA < TCNQ < TCNE ≈ DDQ. EPR spectra of the oxidized binuclear complexes are indicative of localized species containing iron- and carbon-centered radicals. The Mössbauer spectrum of the iodine oxidized complex of **1** reveals the presence of both Fe(III) and Fe(II) centers. Variable temperature magnetic and Mössbauer studies show that the ratio of Fe(III)/Fe(II) centers varies as a function of temperature. The larger Fe(II)/Fe(III) ratio at lower temperatures is best explained by a retro charge transfer from the iodide to the iron(III) metal center. There is negligible solvent effect on the formation of the iodine oxidized charge transfer complex of **1**. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Charge-transfer (CT) complexes of ferrocene and substituted ferrocenes have attracted considerable interest in recent years [1–3]. Potential application of these complexes in superconductivity [4], nonlinear optics [5] and cooperative magnetics [6] have spurred research in this area. In this context, CT complexes of bis(ferrocenyl) complexes should be even more interesting. A number of symmetrical and unsymmetrical binuclear ferrocenes have been investigated [7–12]. The electronic properties of the oxidized binuclear ferrocenes depend on a number of factors including the substitution of the cyclopentadienyl ring and the counter ions. It has been

shown that changing the counter anion in mixed-valence biferrocenium salts leads to dramatic changes in the electron transfer rates in the solid state [13,14]. Recently the effects of acetyl and naphthylimine substituents on the cyclopentadienyl ring and variation of counter anions I₃⁻, CuI₂⁻ and FeCl₄⁻ on the valence state of iron atoms in the biferrocenium derivatives have been reported by Wei et al. [15]. The charge transfer interactions between donor and acceptor moieties have been studied in a series of organometallic complexes derived from organometallic donors and various kinds of acceptors [16–18]. In all these studies, it has been found that small changes in the donor or acceptor, make a significant impact on the electronic properties of the complex.

The present study was aimed at clarifying the effect of varying the acceptors used to form CT complexes of

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N,N'-bis(ferrocenylmethylidene)-*p*-phenylenediamine and *N*-(ferrocenylmethylidene)aniline. Significant differences were observed in the solid complexes formed by I₂, DDQ, TCNE, TCNQ and CA. A unique polyiodide complex is formed by **1**. The valence state of iron in I₂ oxidized compound was studied by Mössbauer spectroscopy, IR and magnetic susceptibility measurements in the solid state. A retro charge transfer in the solid state at low temperatures is proposed, to explain the observed changes in the Mössbauer and magnetic susceptibility data.

2. Experimental details

2.1. Physical measurements

C, H and N analysis of the complexes were obtained from Heraeus Carlo Erba 1168, CDRI, Lucknow and Carlo Erba Strumentazione elemental analyzer—model 1106. Iron percentages of the samples were obtained from ARL, 3410 ICP with minitorch. Iron percentages were also estimated by the standard gravimetric method. The IR spectra of the complexes was recorded either using a Bio Rad FT IR, FTS-7 or a Perkin Elmer 781 double beam spectrometer in the range 400–4000 cm⁻¹ in KBr disc or nujol mull. UV–vis spectra of the complexes were recorded on a Hitachi U-3400 spectrophotometer. The electron spin resonance (ESR) spectra of the complexes were recorded in a X-band Varian E10G line Century series spectrophotometer. ¹H- and ¹³C-NMR spectra of the complexes were recorded using a Bruker ACF 200 FT NMR spectrometer and Jeol FX-90Q spectrometer, respectively. ⁵⁷Fe Mössbauer spectra were recorded with a constant acceleration spectrometer using 25 mCi ⁵⁷Co source in Pd (Amersham, UK) with respect to which isomer shifts (IS) are reported. The spectra were computer-fitted using a general fitting procedure to obtain the best fit to the experimental data. Cyclic voltammograms of the complexes **1** and **2** were recorded in EG&G PAR model 174A polarographic analyzer combined with a standard three electrodes configuration. A platinum or a glassy carbon electrode was used as the working electrode and the counter electrode was a platinum wire. A saturated Calomel electrode was used as a reference electrode. In all electrochemical measurements 0.1 M Bu₄NClO₄ (TBAP) was used as a supporting electrolyte and the redox potentials of the complexes were measured against saturated calomel electrode. EDAX analysis of the complexes were obtained using Cambridge Stereoscan S-360. Magnetic susceptibility measurements were obtained using George Associates Series 300, Lewis coil Tm Force magnetometer.

2.2. Synthesis of

N,N'-bis(ferrocenylmethylidene)-*p*-phenylenediamine
Fc–CH=N–C₆H₄–N=CH–Fc (**1**)

A mixture of ferrocenecarboxaldehyde (2.16 g, 10 mmol) and 1,4-phenylenediamine (0.54 g, 5 mmol), was dissolved in 100 ml dry toluene and refluxed under nitrogen atmosphere with azeotropic removal of water using a Dean–Stark apparatus. After 18 h, the reaction mixture was filtered hot. On cooling a red shiny flaky precipitate was obtained. It was washed with ethanol (3 × 10 ml) and 30 ml of acetonitrile. m.p. 238–240°C. Yield: 93%. [Found: C, 66.96; H, 4.78; N, 5.33. C₂₈H₂₄Fe₂N₂ **1** requires C, (67.23); H, (4.83); N, (5.60%)]. IR (KBr, cm⁻¹): 1613 (CH=N str.), 811 (perpendicular C–H bend of Cp). ¹H-NMR (CDCl₃): 4.26 (s, 10H, C₅H₅), 4.52 (t, 4H, C₅H₄), 4.83 (t, 4H, C₅H₄), 7.30 (s, 4H, C₆H₄), 8.39 (s, 2H, CH=N). ¹³C-NMR (CHCl₃): 69.04 (Cp, s), 68.78 (Cp, α), 71.07 (Cp, β), 121.20 (phenyl, 4C), 150.00 (phenyl, 2C para), 160.83 (CH=N).

2.3. Synthesis of *N*-(ferrocenylmethylidene)aniline

Fc–CH=N–C₆H₅ (**2**)

A mixture of ferrocenecarboxaldehyde, (1.07 g, 5 mmol), aniline (0.57 ml, 6 mmol) and five to ten drops of dry pyridine in 100 ml of dry benzene was refluxed under nitrogen atmosphere with azeotropic removal of water using a Dean–Stark apparatus. After 18 h, the reaction mixture was filtered and cooled. Following the removal of benzene under reduced pressure, the excess of aniline was removed under reduced pressure at a temperature of 100–120°C. After drying the product in vacuum for about 3 h, the crude product was extracted using *n*-pentane in a Soxhlet apparatus. m.p. 70–71°C. Yield: 77%. [Found: C, 70.61; H, 5.22; N, 4.84. C₁₇H₁₅NFe **2** requires C, (70.55), H, (5.19); N, (4.43%)]. IR (KBr, cm⁻¹): 1619 (CH=N str.), 818 (perpendicular C–H bend of Cp). ¹H-NMR (CDCl₃): 4.15 (s, 5H, C₅H₅), 4.35 (t, 2H, C₅H₄), 4.65 (t, 2H, C₅H₄), 6.85–7.40 (m, 5H, C₆H₅), 8.20 (s, 1H, CH=N). ¹³C-NMR (CHCl₃): 68.99 (Cp, s), 68.75 (2,2' Cp), 71.00 (3,3' Cp), 81.10 (1, Cp), 152.57 (α C₆H₅), 124.90 (β C₆H₅), 128.81 (γ C₆H₅), 120.34 (δ C₆H₅), 161.03 (CH=N).

2.4. Preparation of partially oxidized complexes

The Schiff base *N,N'*-bis(ferrocenylmethylidene)-*p*-phenylenediamine **1** and the model compound *N*-(ferrocenylmethylidene)aniline **2** have been oxidized by iodine in benzene, chloroform and ethanol to give **3a–c** and **4a–c**, respectively, to study the effect of solvent polarity on the preparation of partially oxidized compounds.

2.4.1. Synthesis of $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot I_{4.5}$ (**3a-c**)

A solution of iodine (1.52 g, 6 mmol) in 125 ml of benzene was added to the vigorously stirred suspension of compound **1** (2.00 g, 4 mmol) in 150 ml of dry benzene at room temperature (r.t.). The reaction was taken to completion by stirring the mixture for 8 h. A small portion of precipitated iodide (0.44 g) was washed with 2×30 ml portions of chloroform. The solvent was removed under reduced pressure at a bath temperature of 50°C. This yields the major portion of the black polycrystalline iodide (2.00 g) which was washed with chloroform and then dried in vacuum for about 3 h. The combined yield is 84% based on the amount of iodine used. [Found: C, 32.83; H, 2.34; N, 3.03; $C_{28}H_{24}Fe_2N_2 \cdot I_{4.5}$ (**3a**) requires C, (31.39); H, (2.25); N, (2.61%); similarly the complexes $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot I_{4.5}$ (**3b**) and $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot I_{4.5}$ (**3c**) were obtained by employing chloroform and ethanol as reaction mediums, respectively. Their elemental analytical data are as follows: [Found: C, 31.33; H, 2.21; N, 3.35; Fe, 10.33; I/Fe, 2.28 (EDAX). $C_{28}H_{24}Fe_2N_2 \cdot I_{4.5}$ (**3b**) requires C, (31.39); H, (2.25); N, (2.61); Fe, (10.42); I/Fe, (2.25%)] [Found: C, 32.08; H, 2.43; N, 2.78; Fe, 10.65; I/2Fe, 2.35 (EDAX). $C_{28}H_{24}Fe_2N_2 \cdot I_{4.5}$ (**3c**) requires C, (31.39); H, (2.25); N, (2.61), Fe, (10.42); I/Fe, (2.25%)].

2.4.2. Synthesis of $[Fc-CH=N-C_6H_5] \cdot I_{3.5}$ (**4a**) and $[Fc-CH=N-C_6H_5] \cdot I_3$ (**4b,c**)

A solution of iodine (1.90 g, 7.5 mmol) in 100 ml of dry benzene was added slowly to the vigorously stirred solution of **2** (1.45 g, 5 mmol) in 50 ml of dry benzene over a period of 1.5 h and the reaction mixture was stirred at r.t. for 9 h. The reaction mixture was filtered and the solvent was removed under reduced pressure at a bath temperature of 45°C, which afforded the black precipitate. The crude product was washed with *n*-pentane (4×25 ml) and dried in vacuum for 3 h. m.p. 112–115°C. Yield: 73% (decomposition). [Found: C, 27.38; H, 2.18; N, 2.03. $C_{17}H_{15}NFe \cdot I_{3.5}$ (**4a**) requires C, (27.48); H, (2.06); N, (1.91%)]]. Similarly the complexes $[Fc-CH=N-C_6H_5] \cdot I_3$ (**4b**) and $[Fc-CH=N-C_6H_5] \cdot I_3$ (**4c**) were obtained by using chloroform and ethanol as reaction mediums, respectively, and their elemental analytical data are given below. [Found: C, 30.76; H, 2.39; N, 2.14. $C_{17}H_{15}NFe \cdot I_3$ (**4b**) requires C, (30.48); H, (2.25); N, (2.09). (Found: C, 31.45; H, 2.37; N, 1.98; Fe, 8.40; I/Fe, 3.01% (EDAX). $C_{17}H_{15}NFe \cdot I_3$ (**4c**) requires C, (30.48); H, (2.25); N, (2.09) Fe (8.33) I/Fe (3.0%)].

2.4.3. Synthesis of $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot (TCNQ)_2$ (**5**)

Compound **1** (2.00 g, 4 mmol) was dissolved in 120 ml of chloroform. TCNQ (0.82 g, 4 mmol) in 100 ml of THF was added to the above solution dropwise over a

Table 1

Electrochemical data for $Fc-CH=N-C_6H_4-N=CH-Fc$ (**1**) and $Fc-CH=N-C_6H_5$ (**2**) in propylene carbonate with glassy carbon and Pt as working electrode^a

Complex	$E_{1/2}$ (V)		
	Glassy carbon	Pt	
1	0.55	0.54	0.82
2	0.56	0.54	0.92 ^b

^a All $E_{1/2}$ values are relative to SCE.

^b From differential pulse polarography.

period of 3 h. Then the reaction mixture was stirred for 8 h at r.t. and filtered. The filtrate was concentrated and this gave 1.80 g of a green product, which was washed with chloroform to remove unreacted starting material. The yield obtained was 95% based on the amount of TCNQ used. [Found: C, 67.41; H, 3.68; N, 15.76. $C_{52}H_{32}Fe_2N_{10}$ (**5**) requires C, (68.26); H, (4.01); N, (15.86%)].

2.4.4. Synthesis of $[Fc-CH=N-C_6H_5] \cdot (TCNQ)$ (**6**)

N-(Ferrocenylmethylidene)aniline (1.45 g, 5 mmol) was dissolved in 50 ml of acetonitrile. To the above solution, TCNQ (1.02 g, 5 mmol) in 50 ml of acetonitrile was added dropwise over a period of 0.5 h. Then the resulting reaction mixture was stirred and heated to 80°C for 8 h. and then cooled and filtered. The precipitate was washed with chloroform, ether and dried. This

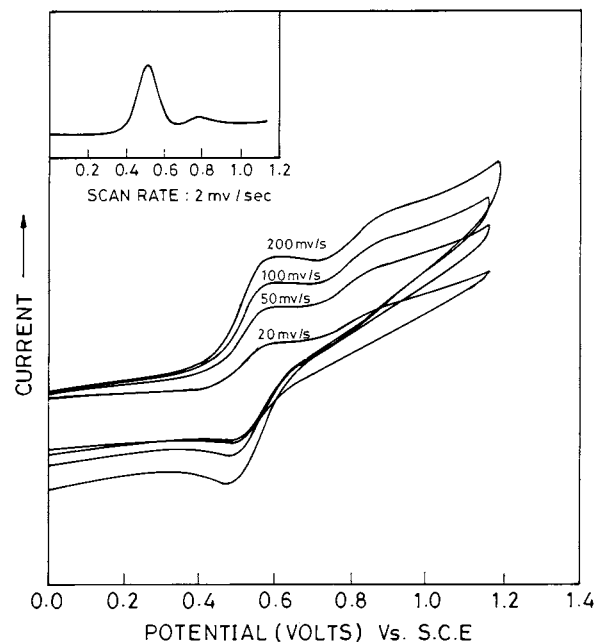


Fig. 1. Cyclic voltammogram and differential pulse voltammogram (inset) of Schiff base complex **1**. Working electrode: Pt; solvent: propylene carbonate.

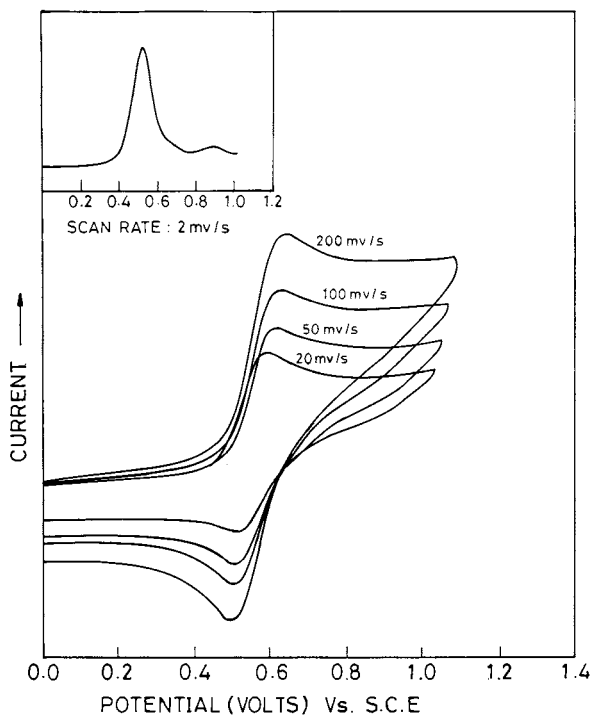


Fig. 2. Cyclic voltammogram and differential pulse voltammogram (inset) of Schiff base complex **2**. Working electrode: Pt; solvent: propylene carbonate.

yields a minor portion of the product (0.30 g). The filtrate was concentrated under reduced pressure and the solid product was washed with chloroform, ether and dried. This yields the major portion of the product (1.20 g). The total yield obtained was 76%. [Found: C, 69.29; H, 4.16; N, 13.72. $C_{29}H_{19}FeN_5$ (**6**) requires C, (70.60); H, (3.88); N, (14.19%)].

2.4.5. Synthesis of $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot (DDQ)_2$ (**7**)

DDQ (0.91 g, 4 mmol) was dissolved in 100 ml of chloroform at 50°C. To the hot solution, compound **1** (1.00 g, 2 mmol) in 100 ml of chloroform was added dropwise over a period of 1 h and the stirring was

Table 2
Electrochemical data for the complex **1**, **2** and different oxidants in different solvents

Complex	$E_{1/2}$ (V)		
	CH ₃ CN	CH ₂ Cl ₂	DMF
1	^a	0.61	0.79
2	0.54	0.61	0.76
I ₂ /I ₃ ⁻	0.61	0.62	0.65
DDQ/DDQ ^{-•}	0.51	0.58	0.59
TCNE/TCNE	0.24	0.54	0.16
TCNQ/TCNQ ^{-•}	0.18	0.47	0.31
CA/CA ⁻	0.03	0.33	0.04

^a Insoluble in CH₃CN.

Table 3
UV-vis data for the Schiff base complexes (**1–12**)

Complex	Solvent	λ_{max} (log ϵ)
1	CHCl ₃	272 (4.50), 350 (4.57), 460 (3.97)
2	CH ₃ CN	281 (4.14), 309 (4.11), 448 (3.34)
3a–c	CH ₃ CN	248 (4.49), 291 (4.83), 363 (4.69), 510 (3.99)
4a–c	CH ₃ CN	243 (4.19), 292 (4.48), 355 (4.32), 525 (3.42)
5	CH ₃ CN	259 (4.38), 393 (4.99), 476 (4.25)
6	CH ₃ CN	374 (4.24), 393 (4.31), 470 (3.93)
7	CH ₃ CN	254 (4.30), 347 (4.13), 417 (3.86), 582 (3.56)
8	CH ₃ CN	253 (4.16), 349 (4.02), 565 (3.13)
9	CH ₃ CN	302 (4.38), 378 (4.48), 479 (4.07)
10	CH ₃ CN	261 (4.26), 367 (4.16), 434 (4.20), 565 (3.52)
11	CH ₃ CN	312 (4.60), 358 (4.61), 393 (4.44), 570 (4.10)
12	CH ₃ CN	273 (4.39), 351 (4.26), 435 (4.05), 560 (3.70)

continued at 60°C for about 8 h. The final reaction mixture was filtered and a black precipitate was obtained. It was washed with chloroform, ether and dried. Yield: 47% (0.89 g). The stoichiometry of the compound obtained was independent of the ratio of **1** and DDQ. [Found for **7**: C, 54.34; H, 2.34; N, 8.51; Fe, 10.64. $C_{44}H_{24}C_{14}Fe_2N_6O_4$ requires C, (55.38); H, (2.53); N, (8.81); Fe, (11.71%)].

2.4.6. Synthesis of $[Fc-CH=N-C_6H_5] \cdot (DDQ)_2$ (**8**)

N-(Ferrocenylmethylidene)aniline (1.45 g, 5 mmol) in 75 ml of chloroform was added dropwise to a stirred suspension of DDQ (1.34 g, 5 mmol) in 100 ml of chloroform. Stirring was continued for 8 h at r.t. and filtered. The black precipitate so obtained was washed with chloroform, ether and dried. The yield obtained was 79% (1.63 g) based on the amount of the DDQ used. [Found for **8**: C, 54.72; H, 2.13; N, 8.4; Fe, 6.52. $C_{33}H_{15}Cl_4FeN_5O_4$ requires C, (53.33); H, (2.03); N, (9.42); Fe, (7.51%)].

2.4.7. Synthesis of $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot (TCNE)_2$ (**9**)

Tetracyanoethylene (0.0317 g, 0.25 mmol) dissolved in 30 ml benzene was added dropwise over a 0.5 h period to a stirred solution of compound **1** (0.060 g, 0.119 mmol) in benzene (15 ml). Stirring was continued at r.t. for 8 h. The black precipitate obtained during the reaction was filtered, washed with benzene and finally dried. The yield obtained was 26.3% (0.025 g) [Found for **9**: C, 63.73; H, 3.45; N, 17.95. $C_{40}H_{24}N_{10}Fe_2$ requires C, (63.51); H, (3.19); N, (18.52%)].

2.4.8. Synthesis of $[Fc-CH=N-C_6H_5] \cdot (TCNE)$ (**10**)

Compound **1** (50 mg, 0.1730 mmol) was dissolved in 20 ml of benzene. Then TCNE (0.022 g, 0.1733 mmol) in 30 ml benzene was added dropwise to the stirred solution of compound **1**. After complete addition stirring was continued at 55–60°C for 10 h. The dark red solid formed was filtered, washed with benzene and

ether and finally air dried. Yield: 22.2% (0.016 g). [Found for **10**: C, 66.42; H, 3.69; N, 16.09. $C_{23}H_{15}N_3Fe$ requires C, (66.20); H, (3.62); N, (16.78%)].

2.4.9. Synthesis of $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot (CA)_2$ (**11**)

Compound **1** (60 mg, 0.119 mmol) was dissolved in 20 ml chloroform. CA (0.0589 g, 0.239 mmol) in 20 ml chloroform was added dropwise to the stirred solution of compound **1**. Stirring was continued at r.t. for 8 h. The color of the solution changes to dark red. The reaction mixture was concentrated under reduced pressure, and the dark red solid which precipitated was filtered, washed with benzene and finally dried. Yield: 26.3% (0.031 g). [Found for **11**: C, 47.77; H, 2.92; N, 2.89. $C_{40}H_{24}N_2Fe_2O_4Cl_8$ requires C, (48.43); H, (2.43); N, (2.82%)].

2.4.10. Synthesis of $[Fc-CH=N-C_6H_5] \cdot (CA)_2$ (**12**)

Tetrachloro-1,4-benzoquinone (CA) (0.085 g, 0.346 mmol) in 30 ml chloroform was added dropwise to the stirred solution of compound **2** (0.050 g, 0.173 mmol) dissolved in 30 ml chloroform. After complete addition the reaction mixture was kept stirred in a water bath maintained at 55–60°C. After 9 h, the solution was concentrated, the black colored solid formed was filtered and washed with chloroform, ether and finally dried under vacuum. Yield: 21.5% (0.029 g). [Found for **12**: C, 45.36; H, 2.11; N, 1.98. $C_{29}H_{15}NFeO_4Cl_8$ requires C, (44.60); H, (1.93); N, (1.79%)].

3. Results

Substituted ferrocenes **1** and **2** were obtained by the condensation of ferrocenecarboxaldehyde with 1,4-phenylenediamine and aniline, respectively using a slightly different procedure from that of Sonogashira et al. [19]. The complexes **3a–c** and **4a–c** were obtained following the literature procedure for the preparation of ferrocenium triiodide [20]. Complexes **1** and **2** are quite stable and highly soluble in common solvents such as toluene, chloroform, benzene and THF, while the iodine oxidized complexes **3a–c** and **4a–c** are soluble only in CH_3CN , THF or DMSO and were freshly prepared as and when necessary. The charge transfer complexes $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot (TCNQ)_2$ **5** and $[Fc-CH=N-C_6H_5] \cdot (TCNQ)$ **6** were obtained by TCNQ oxidation of the complexes $[Fc-CH=N-C_6H_4-N=CH-Fc]$ **1** and $[Fc-CH=N-C_6H_5]$ **2**. Similarly, the complexes $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot (DDQ)_2$ **7** and $[Fc-CH=N-C_6H_5] \cdot (DDQ)_2$ **8** were obtained by oxidation of the complexes **1** and **2**, respectively, with DDQ. Reaction of **1** and **2** with TCNE gives complex $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot (TCNE)_2$ **9** and $[Fc-CH=N-C_6H_5] \cdot (TCNE)$ **10**, respectively. The com-

plexes with CA, $[Fc-CH=N-C_6H_4-N=CH-Fc] \cdot (CA)_2$ **11** and $[Fc-CH=N-C_6H_5] \cdot (CA)_2$ **12** were synthesized by mixing appropriate solutions of **1** and **2** with the acceptor, CA.

3.1. Cyclic voltammetry

The cyclic voltammetry of **1**, and **2** were studied using glassy carbon or Pt working electrodes in various solvents. The cyclic voltammogram recorded in propylene carbonate using a glassy carbon working electrode was quasi-reversible. The electrochemical data of complexes **1** and **2** are given in Table 1. Surprisingly, when Pt disk is used as the working electrode, there are two distinct electrochemical events for complex **1**. Figs. 1 and 2 show the cyclic voltammogram and differential pulse voltammogram of the Schiff base complexes **1** and **2**, respectively using a Pt working electrode and propylene carbonate as the solvent. The half-wave potentials of the first process is 0.54 V and the second anodic peak appears at 0.82 V at a scan rate of 100 $mV s^{-1}$. While the first process is quasi reversible, the second step is irreversible. The separation in the anodic peaks of these two steps is 225 mV. It is tempting to assign these two electrochemical events to the oxidation of the Fe(II)–Fe(II) complex to the mixed-valence Fe(II)–Fe(III) complex, and, at a more positive potential, oxidation to the Fe(III)–Fe(III) complex. Considering the fact that complex **1**, has two well separated Fe atoms, it would be very surprising if there is electronic communication between the two iron centers separated by nearly 12 Å. A better explanation emerges on examination of the CV of the monomer **2** in the same solvent using a Pt working electrode. Complex **2** shows a ferrocenium–ferrocene redox wave with a half potential of 0.54 V. A small separate oxidation of the organic moiety was observed at a more anodic potential 0.92 V versus SCE [21] in the differential pulse polarography. The presence of the second anodic wave in both cases rules out the formation of a mixed valence species in

Table 4
Selected IR stretching frequencies for the CT complexes of iodine, DDQ, TCNE, CA and TCNQ with **1** and **2**

Complex	$\nu_{C=N}$ (cm^{-1})	$\nu_{C=O}$ (cm^{-1})	ν_{C-N} (cm^{-1})	$\perp C-H$ bend (cm^{-1})
3a–c	–	–	1630	823
4a–c	–	–	1633	823
5	2174	–	1641	834
6	2187	–	1646	833
7	2224	1588	1642	833
8	2229	1588	1638	828
9	2198	–	1642	833
10	2205	–	1645	830
11	–	1606	1636	831
12	–	1600	1648	828

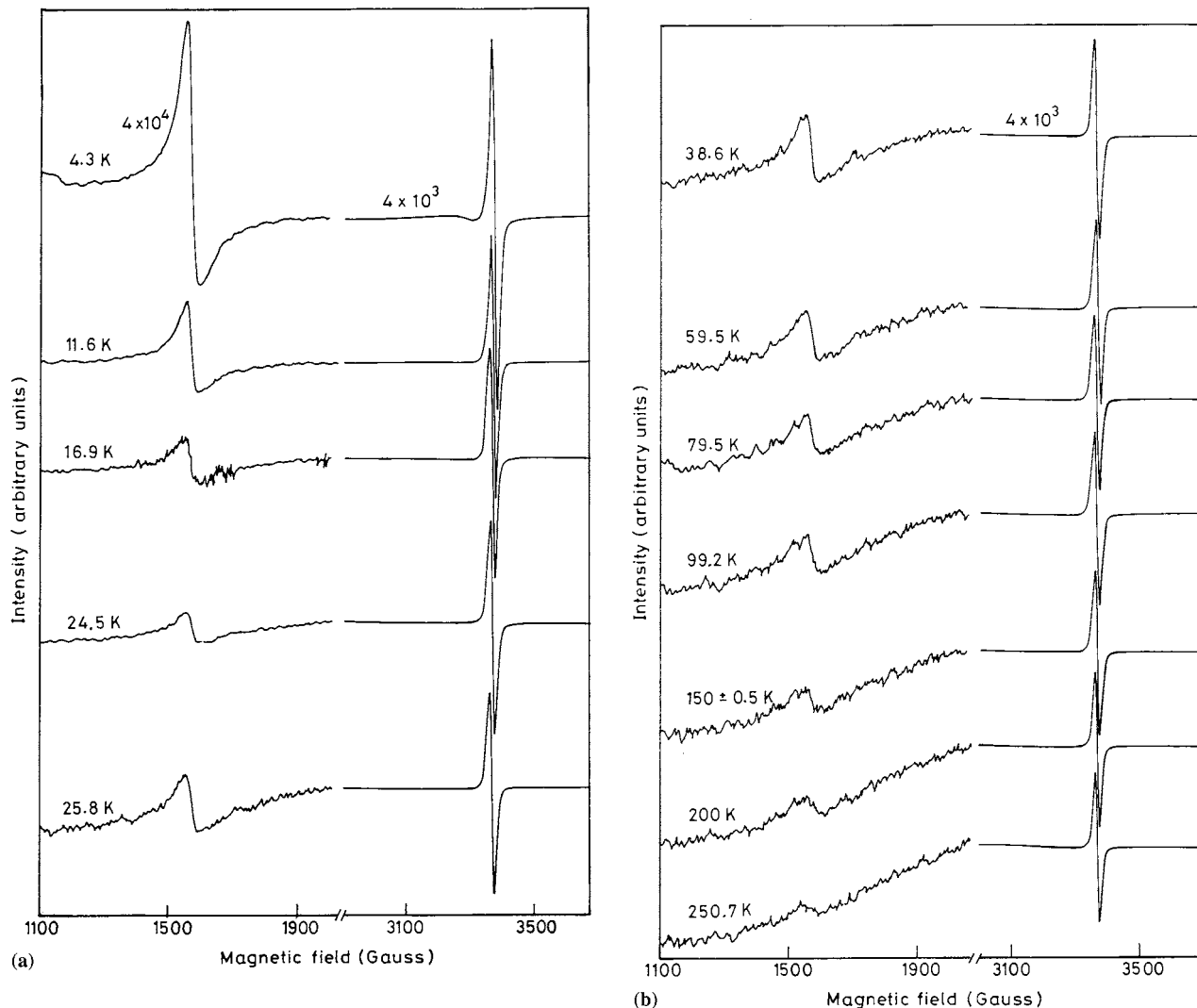


Fig. 3. Variable temperature X-band EPR spectra of $[\text{Fc-CH=N-C}_6\text{H}_4\text{-N=CH-Fc}]\text{I}_{4.5}$ (**3c**).

the oxidation of **1** and suggests that the second wave is due to the Schiff base present in **1** and **2**.

The oxidizing capacity of the acceptors increase in the following order: $\text{CA} < \text{TCNQ} < \text{TCNE} < \text{DDQ} < \text{I}_2$ [22]. No solid complexes were formed when the acceptor oxidation potential was less than 0.01 V versus SCE in acetonitrile. Thus acceptors such as hexafluorobenzene, naphthaquinone and trinitrobenzene do not form solid complexes with **1** and **2**. The more positive the reaction potential, the more favorable would be the formation of an ionic complex. Increase in the polarity of the solvent can also be expected to stabilize an ionic complex. Table 2 gives the redox potentials of the oxidants in acetonitrile, dichloromethane and dimethylformamide solvent mediums.

Although, the redox potentials serve as a guide for predicting the formation of solid complexes between the Schiff bases and the acceptors, other factors affect the extent of charge transfer in these systems and the stoichiometry of the solid complexes formed. The stabi-

lization of the cation formed by the Schiff base in the solid state would depend on the size of the anion due to solid state packing effects as well as the redox potentials. Based on the elemental analysis of the various complexes characterized, it is clear that the CT complexes formed do not have the simple reduced form of the acceptor, A^- , but form larger anions through self complexation such as A_n^- . Although, there is a considerable solvent effect on the oxidation potential of the complexes **1** and **2** on going from CH_3CN to DMF, the stoichiometry and the characteristics of the isolated complexes formed from **1** and **2** were remarkably the same. Variation of solvent polarity did not seem to affect the formation of I_2 oxidized complexes significantly. One exception is the complex formed by **2** with I_2 in benzene. The stoichiometry of this complex **4a** is $2 \cdot \text{I}_{3.5}$ whereas in other solvents the complex formed was only $2 \cdot \text{I}_3$ (**4b,c**). Surprisingly, in spite of this difference in the stoichiometry the spectroscopic properties of the complexes were essentially identical.

Table 5
EPR data of the oxidized Schiff base complexes (3–12)

Complex	g_{\perp} (iron centered)	$g_{(\text{iso})}$ (carbon centered)
[Fc-CH=N-C ₆ H ₄ -N=CH-Fc]I _{4.5} (3c)	4.278	2.006
[Fc-CH=N-C ₆ H ₅]I _{3.5} (4c)	4.280	2.070
[Fc-CH=N-C ₆ H ₄ -N=CH-Fc]·(TCNQ) ₂ (5)	4.230	2.008
[Fc-CH=N-C ₆ H ₅]·(TCNQ) (6)	4.311	1.989
[Fc-CH=N-C ₆ H ₄ -N=CH-Fc]·(DDQ) ₂ (7)	4.112	1.996
[Fc-CH=N-C ₆ H ₅]·(DDQ) ₂ (8)	4.311	2.093
[Fc-CH=N-C ₆ H ₄ -CH=N-Fc]·(TCNE) ₂ (9)	4.169	1.984
[Fc-CH=N-C ₆ H ₅]·(TCNE) (10)	4.135	1.981
[Fc-CH=N-C ₆ H ₄ -N=CH-Fc]·(CA) ₂ (11)	4.007	1.973
[Fc-CH=N-C ₆ H ₅]·(CA) ₂ (12)	4.203	1.988

3.2. Electronic absorption spectra

The electronic spectral data of complexes **1–12** are summarized in Table 3. Neutral Schiff base complexes **1** and **2**, have essentially identical spectra in comparison with related Schiff base complexes [23], and not very different from ferrocene, ferrocenylene and (1,1)-ferrocenophanes [24,25]. In the case of ferrocene and ferrocene compounds there are two bands in the visible region at r.t., which can be assigned to d–d transitions based on their position and intensity. Calabrese et al. [26], reported the visible absorption spectrum of the metallocenes of the form $[M(C_5X_5)\{C_5H_4-(CH=CH)_n-C_6H_4-Y-p\}]$ ($M = \text{Fe}$ or Ru ; $X = \text{Me}$ or H ; $n = 1$ or 2 , $Y = \text{CN}$ or NO_2). These compounds also show two bands in the visible region. The lower energy transition was tentatively assigned to a MLCT and the higher energy transition was assigned to an essentially ligand centered $\pi \rightarrow \pi^*$ transition with some metal character. Based on the over all similarities of these compounds and their absorption spectra to those reported earlier it is reasonable to suppose that molecular orbitals with similar compositions are involved in the electronic transitions of the compounds **1** and **2**.

All partially oxidized Schiff base complexes exhibit multiple bands around 248, 291, 363, 510–532 nm as shown in the Table 3. The band at 535–545 nm is attributed to the ferricenium half of the molecule. The UV spectra of the iodide complexes, **3a–c** and **4a–c** are essentially identical and surprisingly there is no absorption around 700 nm which appears in ferrocenium triiodide. In the case of the binuclear DDQ complex **7**, an additional band probably due to charge transfer is observed at 582 nm.

3.3. Infrared spectra

All the bands characteristic of ferrocene and the Schiff base linkage are observable in the IR spectra of Schiff base complexes **1** and **2**. The characteristic bands

of the CT complexes are shown in Table 4. Our assignments of the various bands observed are based on earlier assignments for ferrocene and related compounds [27]. The perpendicular C–H bending frequency has been considered to be most indicative of the oxidation state of the iron in ferrocene type of compounds [28–30]. The unoxidized Schiff base complexes **1** and **2** show a perpendicular C–H bend at 811 and 818 cm^{-1} , respectively. The strong band observed between 1613 and 1619 cm^{-1} in these complexes is due to the stretching frequency $\nu_{\text{C=N}}$ typical of the Schiff bases. The $\nu_{\text{C=N}}$ of **1** and **2** appear at 1613 and 1619 cm^{-1} , respectively.

The partially oxidized complexes **3a–c** exhibit a single absorption at $823 \pm 3 \text{ cm}^{-1}$. In the case of mononuclear oxidized Schiff base complexes **4a–c** also, a single absorption is seen at $823 \pm 3 \text{ cm}^{-1}$. In the case of the ferrocenium triiodide the perpendicular C–H bend appears at 851 cm^{-1} . The rather small shift in the perpendicular C–H bending of the oxidized complexes **3** and **4** reflects the reduced electron density depletion from the Cp ring of the ferrocene unit. The perpendicular C–H bending vibration appears as a strong band around 833 cm^{-1} for complexes **5–12**. Compared to the iodine oxidized Schiff base complexes, the C–H bend occurs at a higher frequency (by about +10 cm^{-1}) indicating greater amount of charge transfer from the Cp ring to the acceptor in the complexes **5–12**. The C=N stretching frequency also increases on oxidation and follows the same trend as the perpendicular C–H bending vibration. So based on the IR spectral data, the degree of charge transfer from the iron center to the acceptor falls in the following order $I_2 < \text{CA} < \text{TCNQ} < \text{TCNE} \approx \text{DDQ}$.

In the case of Schiff base complexes oxidized by CA, TCNE, DDQ and TCNQ, the presence of additional bands diagnostic of the acceptor C=O and C≡N groups are helpful in understanding the nature of the complexes formed. The ionic nature of the DDQ oxidized complexes **7** and **8** are reflected both in $\nu_{\text{C=N}}$ and $\nu_{\text{C=O}}$ stretching frequencies. DDQ and DDQ^{•-} have $\nu_{\text{C=N}}$

Table 6
Mössbauer data for the neutral Schiff base complexes **1** and **2**

Neutral complex	<i>T</i> (K)	Isomer shift (mm s ⁻¹)	Quadruple splitting (mm s ⁻¹)
Fc-CH=N-C ₆ H ₄ -N=CH-Fc (1)	298	0.459	2.35
Fc-CH=N-C ₆ H ₅ (2)	298	0.456	2.30

and $\nu_{\text{C=O}}$ stretching frequencies at 2233, 1680 cm⁻¹ and 2230, 1600–1580 cm⁻¹, respectively. The $\nu_{\text{C=N}}$ and $\nu_{\text{C=O}}$ stretching vibrations of the complexes fall in the range expected for the DDQ radical anion [30].

The apparent difference in the order of the oxidizing capacity, as measured by the electrochemical potentials and the degree of charge transferred from the Cp ring using the IR technique needs an explanation. In most ferrocenium complexes, it is assumed that the electron is transferred from the iron to the acceptor. However, in complexes such as **1** and **2** where an additional aryl ring is present, electron density could be transferred to the acceptor through the aromatic ring which functions as a donor antenna. Acceptors which overlap with the antenna efficiently allow for greater degree of charge transfer. The changes in the IR stretching frequencies in these complexes appear to be sensitive to the region from which the electron density is removed and not necessarily to the total charge transferred to the acceptor. In the iodine oxidized complexes, the C–H bending frequency changes by small amounts. The shifts in the $\nu_{\text{C=N}}$ are larger, due to their proximity to the site of charge transfer but follow the same trend.

An interesting fact comes to light on examination of the electronic structure of these complexes through extended Hueckel theory (EHT) calculations [31]. Using the program CACAO [32] EHT calculations were carried out on complexes **1** and **2** using the geometrical parameters available for well characterized Schiff bases [23]. The nature of the highest occupied molecular orbital (HOMO) in ferrocene is the d_{z^2} orbital localized on iron. The HOMO in **1** is as expected having considerable contribution from the d_{z^2} orbital of the two iron atoms. But apart from the two iron atoms, the HOMO has significant contributions from the aromatic bridge. Hence, removal of electron density from this molecule is efficiently accomplished by organic acceptors which have LUMOs of the right symmetry and energy to overlap with the aromatic bridge. Even oxidation with iodine in this case occurs by removal of electron density from the aromatic ring and not from the iron as in the case of ferrocenium triiodide. This factor explains the small changes in the perpendicular C–H bending frequency in **3a–c** and **4a–c**.

3.4. Electron paramagnetic resonance spectroscopy

In mixed-valence biferrocenium complexes, it has been found that there is an empirical qualitative correlation of Δg and delocalization [33,34]. A mixed-valence biferrocenium cation which is valence detrapped has a g -tensor anisotropy, $\Delta g < 0.7$, the mixed-valence cation has essentially no potential energy barrier for electron transfer between the two iron centers and is electronically delocalized. Complexes with $\Delta g > 1.5$ have been found to remain valence trapped at all temperatures. The large anisotropy observed in valence localized systems are similar to what is observed for ferrocenium triiodide which exhibits a relatively large anisotropic g -tensor, $g_{\parallel} = 4.35$, $g_{\perp} = 1.26$ and anisotropy, $\Delta g = g_{\parallel} - g_{\perp} = 3.09$ at 20 K [35].

Fig. 3 shows the variable temperature X-band EPR spectrum of the powdered complex [Fc-CH=N-C₆H₄-N=CH-Fc]·I_{4.5} **3c** recorded in the temperature ranges from 4.3 to 290 K. For the complexes **3c** and **4c**, two features are observed. In addition to the iron-centered radical, there was an isotropic signal corresponding to a carbon-centered radical which seem to indicate two different centers are possible for the unpaired electron in these complexes. The intensity of the high field signal for which only the g_{\perp} line is visible was significantly weaker than the isotropic signal at $g = 2.000$. The high field signal has significant intensity only at liquid helium temperature. As the temperature increases, the intensities of the both signals in the complexes **3c** and **4c** decrease drastically without changing their position. For complex **3c** the high field signal completely disappeared at 250 K while for complex **4c**, it disappeared at 290 K. The change in the intensities are presumably due to the change in the spin-lattice relaxation time (T_1) since variable temperature Mössbauer spectra indicate an increase in the concentration of Fe(III) centers at r.t. However, the g -tensor anisotropy of the complexes **3c** and **4c**, could not be computed since the g_{\parallel} line is too weak to be observed.

Powder X-band EPR spectra of the complexes [Fc-CH=N-C₆H₄-N=CH-Fc]·(TCNQ)₂ (**5**), [Fc-CH=N-C₆H₅]·(TCNQ) (**6**), [Fc-CH=N-C₆H₄-N=CH-Fc]·(DDQ)₂ (**7**) and [Fc-CH=N-C₆H₅]·(DDQ) (**8**) were

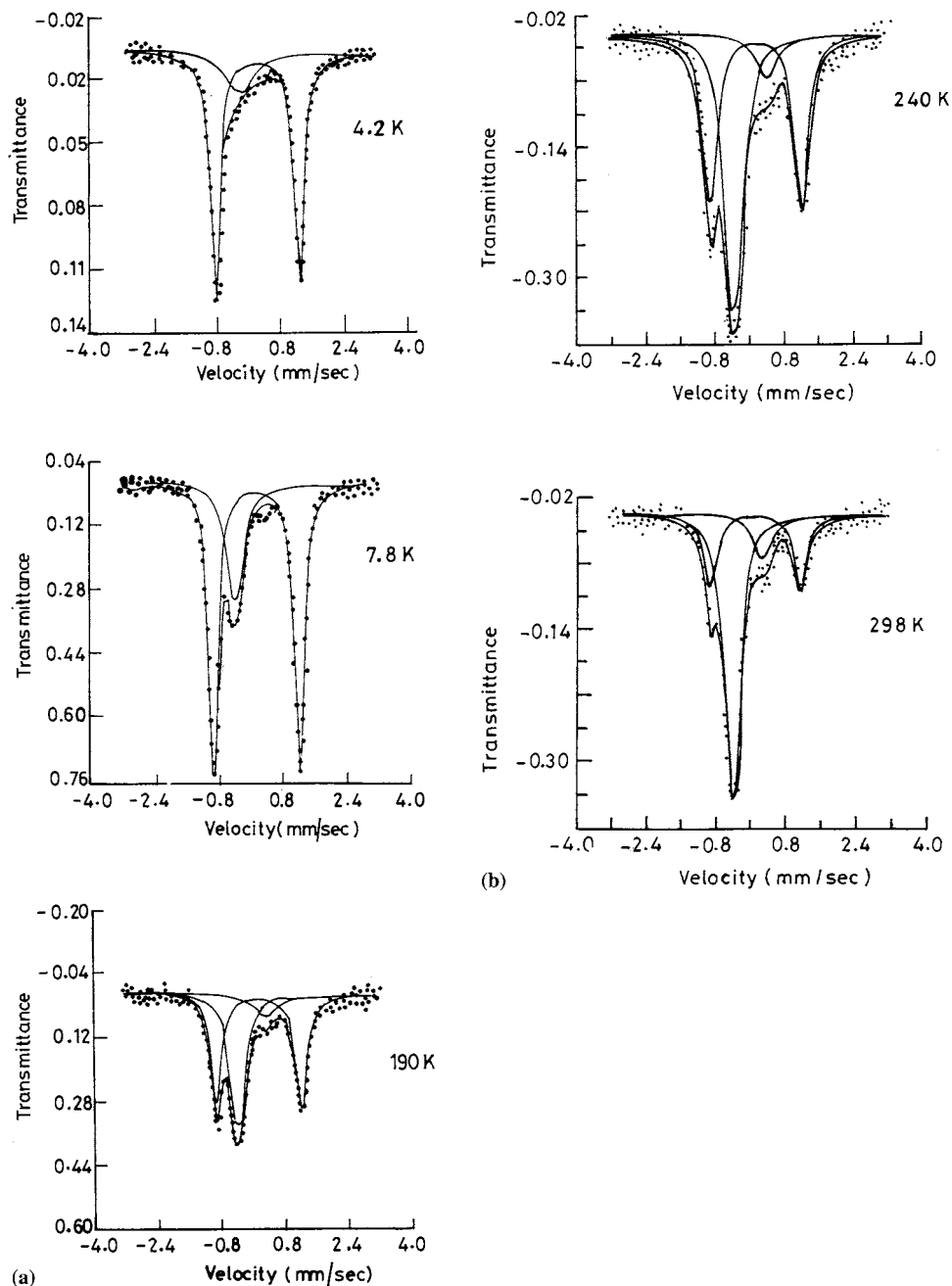


Fig. 4. Variable temperature Mössbauer spectra of $[\text{Fc-CH=N-C}_6\text{H}_4\text{-N=CH-Fc}]_{1.5}$ (**3c**).

recorded at liquid nitrogen temperature (77 K), and are similar. The g values are summarized in Table 5. Similar results are obtained for the CT complexes formed by TCNE and CA.

3.5. Mössbauer and magnetic studies of the iodine oxidized complexes

It has been shown that ^{57}Fe Mössbauer spectroscopy is particularly useful in monitoring the valence state of iron in biferrocenium complexes [36]. The Mössbauer spectrum for a valence trapped biferrocenium cation

shows two quadruple-split doublets, one for Fe(II) ion with a quadruple splitting $\Delta E_q = 2.1 \text{ mm s}^{-1}$ and the other for Fe(III) ion with ΔE_q in the range 0–0.5 mm s^{-1} . If the mixed-valence biferrocenium cation is de-trapped that is, it is interconverting at a rate in excess of 10^7 to 10^8 s^{-1} , then a single doublet with average properties ($\Delta E_q = 1.1 \text{ mm s}^{-1}$) is seen. The Mössbauer spectra of the unoxidized complexes were as expected for substituted ferrocene complexes. The data for complexes **1** and **2** are given in Table 6.

Variable temperature ^{57}Fe Mössbauer spectrum of the iodine oxidized complex **3c** $[\text{Fc-CH=N-C}_6\text{H}_4\text{-}$

Table 7
Mössbauer data for $[\text{Fc}-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{Fc}]\cdot\text{I}_{4.5}$ complex **3c**

<i>T</i> (K)	Fe(II)				Fe(III)			
	IS (mm s ⁻¹) ^a	EQ1 (mm s ⁻¹) ^b	<i>B</i> (mm s ⁻¹) ^c	<i>I</i> ₁ (%) ^d	IS (mm s ⁻¹)	EQ1 (mm s ⁻¹)	<i>B</i> (mm s ⁻¹)	<i>I</i> ₂ (%)
4.2	0.255(8)	2.18(1)	0.31(1)	88.1(5)	-0.168(8)	0.359(8)	0.36(1)	7.9(7)
20.0	0.250(8)	2.18(1)	0.30(1)	86.0(5)	-0.188(8)	0.395(8)	0.38(1)	10.5(7)
79.0	0.251(8)	2.17(1)	0.28(1)	77.7(5)	-0.207(8)	0.195(8)	0.38(1)	16.4(7)
145.0	0.238(8)	2.17(1)	0.28(1)	60.7(7)	-0.240(8)	0.133(8)	0.38(1)	25.4(5)
190.0	0.230(8)	2.13(1)	0.32(1)	49.8(7)	-0.288(8)	0.160(8)	0.34(1)	41.0(5)
250.0	0.221(8)	2.16(1)	0.30(1)	38.0(7)	-0.228(8)	0.176(8)	0.37(1)	55.0(5)
295.0	0.313(8)	2.05(1)	0.33(1)	27.4(7)	-0.231(8)	0.170(8)	0.41(1)	63.0(3)

<i>Fe(II) high-spin contamination</i>				
<i>T</i> (K)	IS (mm s ⁻¹)	EQ1 (mm s ⁻¹)	<i>B</i> (mm s ⁻¹)	<i>I</i> ₂ (%)
79.0	1.45(1)	2.17(1)	0.35(1)	5.9(7)
250.0	1.40(1)	1.91(1)	0.35(1)	7.0(7)

^a IS, isomer shift → Fe(Rh).

^b EQ, quadruple splitting.

^c *B*, line-width.

^d *I*, intensity ratio.

$\text{N}=\text{CH}-\text{Fc}\cdot\text{I}_{4.5}$ is shown in Fig. 4. This spectra was least square fit with Lorentzian line shapes, the spectral fitting parameters for the complex is given in Table 7. The ⁵⁷Fe Mössbauer spectrum of this complex was collected at six temperatures between 4.2 and 295 K. At 4.2 K, ⁵⁷Fe Mössbauer spectra shows quadruple doublets corresponding to Fe(II) center (88%) (IS = 0.255 mm s⁻¹, QS = 2.18 mm s⁻¹) with a small amount of

an Fe(III) ferromagnetic impurity. As the temperature increases, the intensity of the inner quadruple doublets corresponding to the Fe(III) center increases with decrease in intensity of the Fe(II) center. At 190 K, both Fe(II) and Fe(III) quadruple doublets have almost equal intensity. At r.t., the inner quadruple doublets corresponding to Fe(III) has very high intensity (63%) compared to the Fe(II) center (27.4%). This suggests that at low temperature (4.2 K), the complex undergoes a retro charge-transfer from the polyiodide anion I_n^- to the ferrocenium part of the molecule [37].

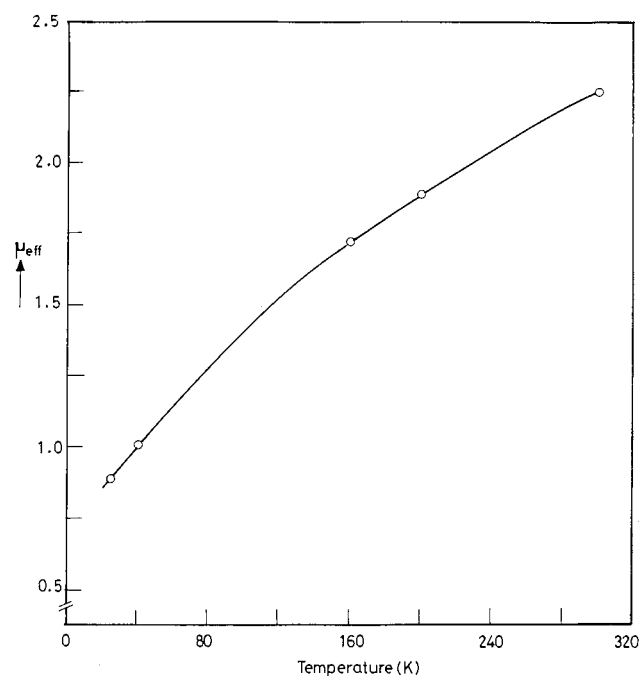
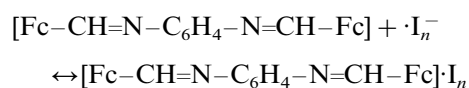


Fig. 5. Magnetic moment (BM) versus temperature (K) plot of $[\text{Fc}-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{Fc}]\cdot\text{I}_{4.5}$ (**3c**).

Magnetic susceptibility studies confirm that such a retro charge transfer is occurring at low temperatures. The calculated magnetic moment for the iodine oxidized complex is less than that expected for the fully oxidized (3,3) complex but greater than that computed for a (2,3) complex. The effective magnetic moment decreases with decrease in temperature as expected for a complex in which retro charge transfer is taking place. The magnetic moment calculated from the susceptibility as a function of temperature for the iodine oxidized complex is given in Fig. 5. In principle, the reduced magnetic moment at low temperatures could also be explained by invoking antiferromagnetic coupling. If this was true, Curie-Weiss behavior would be expected and a plot of χ^{-1} versus temperature would be linear. Since this is not the case, retrocharge transfer appears to be a more suitable explanation for the change in the magnetic moment as a function of temperature.

4. Conclusion

The Schiff base complexes **1** and **2** form interesting charge transfer complexes with a variety of acceptors. The solution state redox potentials of the complexes and the oxidants are not indicative of the type of complex that could be formed in the solid state but could be used to provide a guide for the synthesis of solid CT complexes. The size, shape and charge distributions of the acceptors used in this study are completely different, and all of these factors are ultimately important in determining the stoichiometry, charge transfer and other properties of the isolated complexes. IR spectra of the complexes reveal the extent of charge transfer in these complexes and suggest the regions of electron density depletion. Mössbauer spectroscopy of the iodine oxidized complexes is interesting. Surprisingly, it shows the presence of both oxidized and unoxidized iron centers. The ratio of these two species is temperature dependent and a retro charge transfer is indicated at low temperatures. The extent of electron density transferred from the biferrocene to the oxidant is determined by the nature of complex formed in the solid state, which in turn is critically dependent, among other things, upon the nature of the HOMO and the size of the anion formed. Since oxidation removes an electron from a MO having significant contributions from the aromatic spacer, organic acceptors are more efficient in removing electron density from **1** and **2**.

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