JOURNAL OF
Materials
CHEMISTRY

New radical salts of diferrocenyl-VT (VT: bis(vinylenedithio)tetrathiafulvalene)

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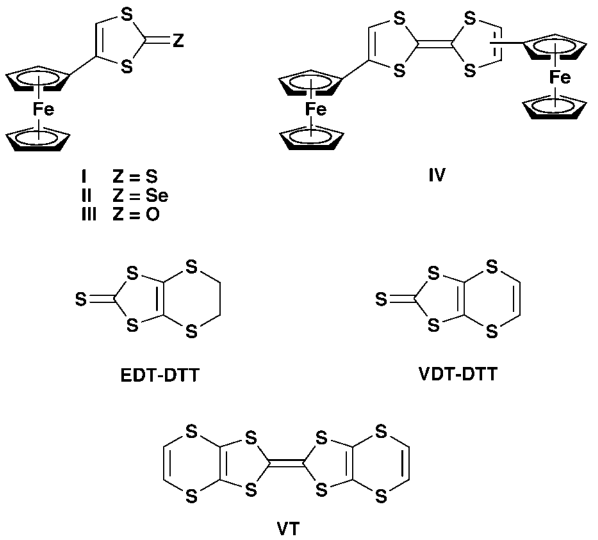
Received 6th April 1999, Accepted 6th August 1999

1,1′-Diferrocenyl-VT **5** is successfully prepared by phosphite-based coupling reaction of ferrocenyl 1,3-dithiol-2-one **4**. It shows one reversible cyclic voltammogram with $E_{pa} = 0.66$ V and forms radical cation salts with I_3^- and BF_4^-. In compound **5·(I₃)**, according to the temperature-controlled EPR and Mössbauer measurements, the VT moiety is oxidised to form a radical, while the two ferrocene groups are not oxidized. In compound **5H·(BF₄)₄**, however, a mixed ferrocene/ferrocenium system consisting of low-spin Fe(II), high-spin Fe(II) and Fe(III) is detected by Mössbauer spectroscopy. Due to the protonation of VT by HBF_4, the extended π-electron system of VT is degraded into the TTF system. The electrical conductivities of pressed pellets of the radical cationic salts are 7×10^{-3} S cm^{-1}.

Recently, many ferrocene-containing materials have been widely studied in the area of molecular electronics because ferrocene shows a versatile Fe(II)/Fe(III) redox property.[1–6] The investigations of intramolecular electron transfer in mixed-valence systems have received special focus. The combination of ferrocene with a multisulfur compound offers a new sulfur-based synthon for the preparation of molecular materials with unusual solid-state properties such as enhanced electrical conductivity, unusual magnetic behavior and non-linear optical (NLO) effects.[1] Ferrocenyl 1,3-dithiole compounds **I–III** have been developed as precursors to ferrocenyl multisulfur compounds, with which diferrocenyl-TTF (**IV**)[4] was prepared as well as the related nickel–bisdithiolene complex[2] (Scheme 1). Compound **IV** formed a 1 : 1 charge-transfer complex with DDQ (2,3-dichloro-5,6-dicyanobenzo-1,4-quinone), with electrical conductivity at room temperature of 1×10^{-3} S cm^{-1}.

The extension of the multisulfur system present in TTF by the addition of external six-membered rings gives VT which is regarded as an attractive donor molecule with a totally planar structure. VT gives conductive radical cation salts with I_3^- (160 S cm^{-1})[7] and PF_6^-(20 S cm^{-1})[8] anions. Only a few VT-derivatives have been reported[7,9] among which the triiodide salt of tetramethyl-VT was recorded as having a metallic conductivity of 60 S cm^{-1}. Even though VT and its derivatives yielded some metallic salts, little attention was focused on them mainly because VT derivatives with various functional groups were not easily synthesised.



Scheme 1

As a result of extensive research[2,3,10] on the development of new functional multisulfur compounds based on EDT-DTT (4,5-ethylenedithio-1,3-dithiole-2-thione) and VDT-DTT (4,5-vinylenedithio-1,3-dithiole-2-thione) (Scheme 1), we have previously reported the synthesis and chemistry of a phenyl-substituted EDT-DTT.[10a] These compounds were readily prepared by a [2+4] cycloaddition reaction, which has also been applied to prepare the ferrocenyl compounds described in this paper. Here, we report the synthesis and properties of ferrocene-containing EDT-DTT **2** and VDT-DTT **3**. By using **3** or its oxo-analogue as a coupling reaction precursor, the first diferrocenyl-VT **5** was successfully prepared in which two ferrocene moieties are directly linked to the VT moiety. Radical cation salts of **5** with BF_4^- and I_3^- were prepared and investigated with temperature-controlled EPR and Mössbauer spectroscopy measurements. The electrical conductivities of these radical cation salts were also measured.

Experimental

Elemental analysis and EPR measurements were carried out at the Korea Basic Science Institute (KBSI), all mass spectroscopic analysis at the EPSRC National Mass Spectrometry Service Centre (Dept. of Chemistry, University of Wales, Swansea, UK). Melting points were determined using an electrothermal digital melting point apparatus IA9100 without calibration. NMR spectra were recorded on a Bruker AC-250 spectrometer, infrared spectra by the KBr method on a Perkin-Elmer 1600 series instrument and UV spectra in acetonitrile on an HP 8452A diode array spectrometer. Cyclic voltammetric measurements were carried out at room temperature with an EG&G VersaStat model Potentiostat/Galvanostat in 20 ml CH_3CN solution containing 0.1 M n-$Bu_4N \cdot BF_4$ as electrolyte, Ag/AgCl as a reference electrode, a Pt-button working electrode, platinum wire as a counter electrode, and a 0.05 V s^{-1} scan rate. The sample concentration was 5 mM.

Mössbauer spectra were recorded using a conventional Mössbauer spectrometer of the electromechanical type with a 10 mCi ^{57}Co source in a Rh matrix which oscillated in a sinusoidal mode. In order to produce a uniform thickness over the area of the Mössbauer absorber, each sample was mixed with boron nitride powder. The area density of Fe for the flattened sample was 10 mg cm^{-2}. The spectrometer was calibrated with a 25 μm thick α-Fe foil.[11]

5,6-Dihydro-5-ferrocenyl-1,3-dithiolo[4,5-*b*][1,4]dithiine-2-thione: 2

A 10 ml benzene suspension of the oligomeric trithione[12] (844 mg, 4 mmol) and vinylferrocene **1** (212 mg, 1 mmol) in a 25 ml quartz tube was irradiated by UV light of 254 nm with stirring at room temperature. The reaction solution became transparent after 2 h, and then was filtered and decolourized over activated carbon for 20 min and then evaporated to dryness. The product was purified by column chromatography on a silica gel support using chloroform as an eluent and crystallized from $CHCl_3$–MeOH. To obtain single crystals for X-ray analysis, the product was dissolved in acetone and stored in a freezer. The same product can be obtained by refluxing the reaction mixture instead of using UV-irradiation. Yield: 94%; Mp: 127–128 °C; E.A. for $C_{15}H_{12}S_5Fe$: calc. C 44.13, H 2.96, S 39.19%, obs. C 44.15, H 2.72, S 38.34%; EIMS (*m*/*z*): 408(M$^+$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.30 (2H, CH_2, m), 4.24 (2H, C_5H_4, m), 4.26 (5H, C_5H_5, s), 4.28 (2H, C_5H_4, m), 4.60 (1H, CH, m); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 36.712, 45.889, 67.022, 67.374, 68.757, 68.942, 69.251, 121.750, 126.639, 208.425; FT-IR (KBr, cm^{-1}): 1485.8, 1458.3, 1405.9 (C=C), 1254.0, 1104.6, 1066.9 (C=S), 1040.0, 999.4, 910.8, 895.7, 840.3, 826.1, 807.8, 689.4, 496.7, 481.6 (Fc); UV (CH_3CN, nm): 211(st), 273(m), 411(m).

5-Ferrocenyl-1,3-dithiolo[4,5-*b*][1,4]dithiine-2-thione: 3

A 20 ml benzene solution of compound **2** (350 mg, 0.86 mmol) and DDQ (195 mg, 0.86 mmol) was refluxed for 30 min with stirring. After cooling to room temperature, the solid in the reaction mixture was filtered off and washed with a small amount of hot benzene. The combined benzene solutions were decolourized over activated carbon for 20 min and evaporated under reduced pressure. The shiny brick-red crystals were recrystallized from $CHCl_3$–MeOH. For the analytical samples, this compound was purified further by column chromatography on a silica gel support using chloroform as an eluent. Yield: 77–83%; Mp: 197–198 °C; EIMS (*m*/*z*): 406(M$^+$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.25 (5H, C_5H_5, s), 4.38 (2H, C_5H_4, t), 4.50 (2H, C_5H_4, t), 6.29 (1H, CH, s); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 67.846, 69.815, 70.354, 80.702, 110.628, 141.990, 213.879; FT-IR (KBr, cm^{-1}): 1560.2, 1484.7, 1383.8 (C=C), 1257.3, 1103.9, 1062.4 (C=S), 1031.4, 1000.6, 903.9, 847.9, 813.9 (Ar C–H), 476.3 (Fc); UV (CH_3CN, nm): 200(s), 243(sh), 288(m), 392(m).

5-Ferrocenyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-one: 4

To a 50 ml $CHCl_3$ solution of compound **3** (0.81 g, 2 mmol) was added acetic acid (50 ml) and $Hg(OAc)_2$ (1.27 g, 4 mmol), and the mixture was stirred for 30 min at room temperature. The white precipitate was filtered off, and the filtrate was washed with H_2O, saturated aq. $NaHCO_3$, finally with H_2O and then dried over Na_2SO_4. After evaporation of solvent under reduced pressure, the residue was purified by column chromatography on a silica gel support using chloroform as an eluent. Yield: 58–64%; Mp: 134–135 °C; FT-IR (KBr, cm^{-1}): 1670.5 (C=O), 1631.9, 1500.7, 1454.4 (C=C), 1259.6, 1107.2, 1051.3, 1030.1, 1003, 947.1, 904.7, 873.8, 829.4, 806.3, 775.4, 744.6 (Ar C–H), 715.6, 694.4, 640.4, 532.1, 517, 480.3 (Fc); UV (CH_3CN, nm): 218(st), 234(st), 286(m), 448(vw).

Coupling reaction of 4 to give 5

Compound **4** (300 mg, 0.77 mmol) was dissolved in freshly distilled $P(OEt)_3$ (2.2 ml) and refluxed for 30 min. The dark-red solution was cooled to room temperature, 10 ml of MeOH were added, and the mixture was stored in a freezer. The orange plate microcrystals which were formed were filtered and washed with cold MeOH. The crude product was recrystallized from CH_2Cl_2–MeOH (1 : 1). Yield: 66%; Mp: >240 °C (decomp.); EIMS (*m*/*z*): 748(M$^+$); FABMS (*m*/*z*): 748(M$^+$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.23 (5H, C_5H_5, s), 4.34 (2H, C_5H_4, t), 4.48 (2H, C_5H_4, t), 6.28 (1H, CH, s); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 67.216, 67.602, 69.753, 70.005, 112.044, 137.045; FT-IR (KBr, cm^{-1}): 3098.2, 3038.9, 2923.9, 1559.9, 1384.4 (C=C), 1253.9, 1104.0, 1049.1, 1027.3, 1000.4, 946.3, 910.6, 828.3, 763.5 (Ar C–H), 741.2, 669.7, 643.5, 622.1, 531.2, 491.2, 478.9 (Fc), 419.9; UV (CH_3CN, nm): 200(s), 233(sh), 289(m), 332(sh).

Radical cation salts of 5

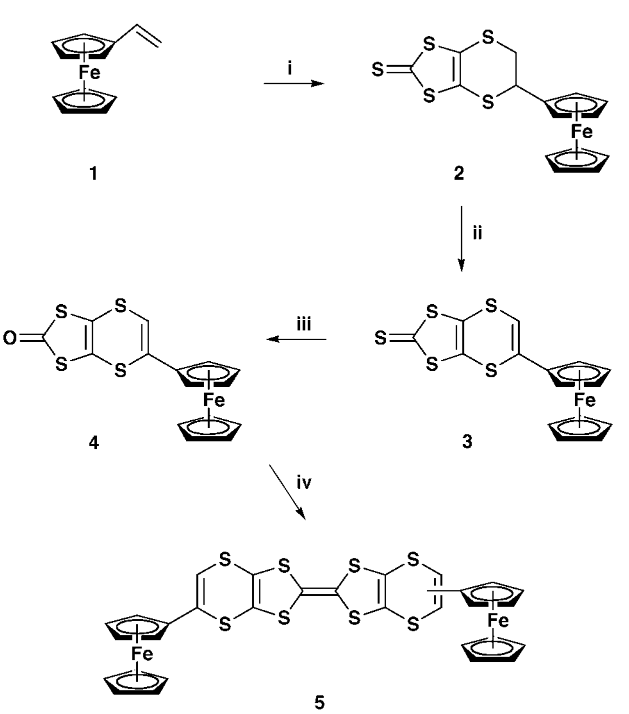
5·(I$_3$). To a 25 ml CH_2Cl_2 solution of compound **5** (75 mg, 0.1 mmol) was added a 15 ml CH_2Cl_2 solution of iodine (38 mg, 0.3 mmol), and the mixture was stirred with heating for 20 min. A black precipitate formed as the reaction solution cooled down to room temperature. The black charge-transfer complex was filtered off, washed with CH_2Cl_2 and dried under vacuum. Yield: 59%; E.A. for $C_{30}H_{20}S_8Fe_2I_3$: calc. C 31.90, S 22.66%, obs. C 32.82, S 22.12%; FT-IR (KBr, cm^{-1}): 1427.4 (C=C), 1200, 1105.3, 1001.1, 895, 848.7, 827.5, 491.9; UV (CH_3CN, nm): 212(m), 228(sh), 292(s), 356(m).

5H·(BF$_4$)$_4$. To a stirred solution of benzo-1,4-quinone (8 mg, 0.073 mmol) in 5 ml diethyl ether was added 0.02 ml ethereal solution of HBF_4 (54%, 0.145 mmol). A benzene solution of compound **5** (36.5 mg, 0.05 mmol) was added to the ethereal mixture and the mixture was stirred for 20 min. The black precipitate formed was filtered, washed with benzene and dried under vacuum. Yield: 51%; E.A. for $C_{30}H_{21}S_8Fe_2B_4F_{16}$: calc. C 32.85, S 23.34%, obs. C 33.47, S 23.25%; FT-IR (KBr, cm^{-1}): 1431.3 (C=C), 1122.6, 1105.3, 1084.1, 1062.8, 1035.8, 1003, 879.6, 823.7, 489.9; UV (CH_3CN, nm): 200(sh), 234(s), 254(s), 292(s), 336(sh).

Results and discussion

Synthesis

As a precursor for ferrocenyl VT compounds, **3** and its oxo-analogue **4** were prepared as outlined in Scheme 2. Compound **2** was obtained *via* a Diels–Alder type [2+4] cycloaddition reaction of oligomeric 1,3-dithiole-2,4,5-trithione, $[C_3S_5]_n$,[12] and commercially available vinylferrocene **1**. Treatment of **2** with DDQ yielded the totally π-electron connected compound **3** as a result of the deprotonation on C(sp^3). Attempts to prepare the oxo-analogue of **2** by using $Hg(OAc)_2$ in $CHCl_3$ only resulted in the decomposition products (compound **1** and an unidentified yellow solid). The coupling reaction by refluxing **2** and freshly distilled $P(OEt)_3$ in toluene was tried in order to prepare diferrocenyl-ET. It was also unsuccessful and only the decomposition product **1** was isolated by silica-gel column chromatography and confirmed by FT-IR. It suggests that the S–C(sp^3) bond is the most susceptible to bond cleavage in this compound. The oxo compound **4** was obtained from compound **3** by using $Hg(OAc)_2$ in $CHCl_3$ (60% yield). Treatment of **4** in neat refluxing $P(OEt)_3$ afforded the diferrocenyl-VT **5** in 66% yield. This is the first VT compound in which a conjugated link between two ferrocenes and VT is directly incorporated. It is also an extension of the multisulfur system of compound **IV**. Even though a needle-shaped crystal of **5** was grown in concentrated $CHCl_3$ solution, it was not



Scheme 2 *Reagents and conditions*: i, oligo(1,3-dithiole-2,4,5-trithione), benzene, reflux or *hν* (254 nm), 2 h; ii, DDQ–benzene, reflux, 0.5 h; iii, $Hg(OAc)_2$; iv, neat $P(OEt)_3$, reflux, 0.5 h.

suitable for X-ray analysis probably because the molecules exist as a mixture of possible isomers.

Electrochemical properties

Electrochemical properties for the ferrocenyl multisulfur compounds (**2**, **3** and **5**) prepared in this study as well as those for ferrocene and vinylferrocene **1** were measured by cyclic voltammetry in CH_3CN (0.1 M n-$Bu_4N{\cdot}BF_4$, Pt electrode, Ag/AgCl) and are listed in Table 1. The ferrocenyl multisulfur compounds all exhibit only one redox cycle. A representative cyclic voltammogram of **5** for the three compounds is shown in Fig. 1. Anodic peak potentials (E_{pa}) for the three multisulfur compounds are higher than that of ferrocene, especially for compounds **3** and **5** in which ferrocenes are linked to the multisulfur moiety by π-connection. It suggests that multisulfur moieties act as electron-withdrawing groups and therefore destabilize the ferrocenium cation. The differences between anodic and cathodic peak potentials (ΔE) are all equal at 0.10 V for the three ferrocenyl multisulfur compounds. This is smaller than that of ferrocene (0.12 V) and vinylferrocene (0.13 V). This fact indicates that the voltammograms obtained are predominantly attributed to a redox process of the ferrocenyl groups. Compound **5** is composed of three redox active units: two ferrocenes and the bridging VT. Only one reversible potential peak, however, is obtained as shown in Fig. 1, because the two ferrocenes are weakly coupled through a bridging VT with a π-electron system long enough. As known for the diferrocenylpolyene system, two ferrocenes separated by a long π-conjugation system are weakly coupled and give rise to only one redox peak.[13]

Table 1 Electrochemical properties of ferrocenyl compounds[a]

Compounds	E_{pa}/V	E_{pc}/V	ΔE/V[b]
Ferrocene	0.49	0.37	0.12
1	0.53	0.40	0.13
2	0.63	0.53	0.10
3	0.68	0.58	0.10
5	0.66	0.56	0.10

[a] Sample conc. 1 mM with 0.1 M $TBA{\cdot}BF_4$ in 10 ml CH_3CN, scan rate 0.05 V s^{-1}, ref. to Ag/AgCl. [b] $\Delta E = E_{pa} - E_{pc}$.

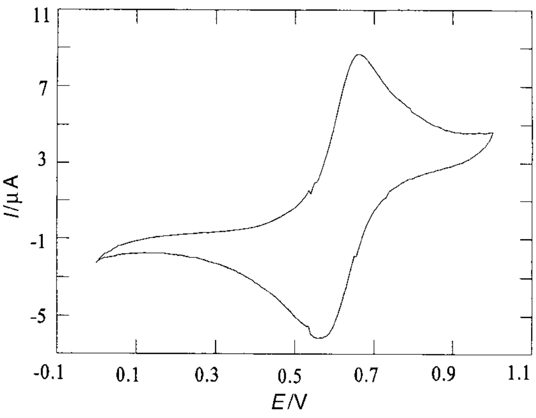


Fig. 1 Cyclic voltammogram of compound **5**.

Radical cation salts

The polyiodide complex of **5** was prepared by mixing hot CH_2Cl_2 solutions of **5** and iodine. As the mixed CH_2Cl_2 solution was cooled down to room temperature, a black precipitate formed, the composition of which was determined to be **5**: $I_3 = 1:1$ based on elemental analysis. Single crystals suitable for X-ray structural analysis or conductivity measurement were not obtained probably because compound **5** is a mixture of *cis*- and *trans*-isomers. The tetrafluoroborate complex of **5** was also prepared following the same procedure by using HBF_4 ethereal solution. The molar ratio of **5** to BF_4^- was determined to be 1 : 4. These mole ratios are very different from other VT complexes such as $VT(I_3)_{0.4}$[7] and $VT(PF_6)_{0.5}$,[8] indicating that substituted ferrocenes play an important role in determining the oxidation state of compound **5**.

Temperature-controlled EPR and Mössbauer spectra of compound **5** and its salts were measured, collected parameters of which are shown in Table 2. The polyiodide compound

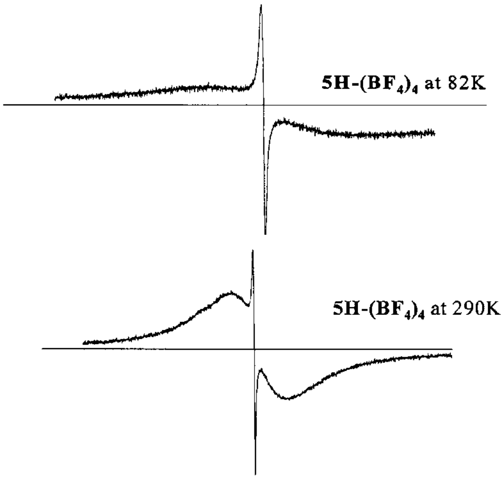


Fig. 2 EPR spectra of $5{\cdot}(I_3)$ at 82 K (top) and $5H{\cdot}(BF_4)_4$ at 82 K (middle) and 290 K (bottom).

Table 2 ^{57}Fe Mössbauer and EPR parameters for compound **5** and its radical salts at various temperatures

Parameters	**5**		**5·(I$_3$)**		**5H·(BF$_4$)$_4$**								
T/K	82	290	82	290	82			150			290		
δ/mm s^{-1a}	0.54	0.47	0.55	0.46	0.502	1.45	0.59	0.60	1.35	0.43	0.61	1.28	0.45
ΔE_Q/mm s^{-1}	2.35	2.36	2.35	2.33	31	3.19	0.42	2.26	2.92	0.70	2.28	3.23	0.69
Intensity %	100	100	100	100	38	41	21	24	24	52	17	17	66
Valence state^b	Fe(II) LS	Fe(II) LS	Fe(II) LS	Fe(II) LS	Fe(II) LS	Fe(II) HS	Fe(III) HS	Fe(II) LS	Fe(II) HS	Fe(III) HS	Fe(II) LS	Fe(II) HS	Fe(III) HS
T/K	82	290	82	290	82		290						
g	^{c}	^{c}	2.006	2.006	2.009	2.006	2.010	2.006					
ΔH/G	—	—	16	27	16	400	17	378					

$^a\delta$ is relative to Fe metal. ^{b}LS: low-spin state; HS: high-spin state. ^{c}No signal detected.

exibits one sharp EPR-signal ($g=2.006$) typical of a free radical[14] at 82 K as shown in Fig. 2, and at 290 K (not shown) as well, compared to the EPR-silent behavior of compound **5**. This suggests that the VT moiety is oxidized to a radical cation by reaction with iodine whilst the ferrocenes remain unchanged, that is in the low-spin Fe(II) state. This is further supported by Mössbauer spectra of **5** and **5·(I$_3$)** (Fig. 3) which contain one quadrupole doublet with isomer shift (δ) and quadrupole splitting (ΔE_Q) values corresponding to ferrocene (Table 2) for both compounds.

$$\text{Fc–[VT]–Fc} \xrightarrow{\text{I}} (\text{Fc–[VT]}^{\bullet+}\text{–Fc})\bullet(\text{I}_3)^-$$

On the contrary, Mössbauer spectra of **5H·(BF$_4$)$_4$** consist of three quadrupole doublets at all temperatures measured (Fig. 4) corresponding to low-spin Fe(II), high-spin Fe(II) and Fe(III) species. That is, a mixed valence state including an unusual high-spin ferrocene is detected.

When compound **5** was treated with HBF$_4$, the external –CH= unit is likely to be most susceptible to electrophilic attack (H$^+$ in this case), in which protonation is achieved by forming a resonance equilibrium between **5A** and **5B** (Scheme 3). Ferrocene in **5A** would remain in the low-spin state Fe(II) upon protonation. In **5B**, the cyclopentadienyl ring (Cp) directly linked to the VT moiety could be changed to cyclopentadiene. Influenced by this modification of the Cp ring, the e$_{1g}$ level in ferrocene will decrease in energy because the interactions between the e$_{1g}$ orbital of Cp and the metal 3d$_{xz}$ or 3d$_{yz}$ orbitals could be weakened.[15] Consequently, the high-spin state Fe(II) would be possible in **5B** and the intensity ratio of high-spin and low-spin states very close to unity at any temperature measured (Table 2) when the stabilities of **5A** and **5B** are equal.

The concentration of Fe(III), derived from least-squares fitting to the Mössbauer spectra, is 21% at 82 K and increases up to 66% at 290 K, indicating that the population of ferrocenium increases as the temperature goes up. This is consistent with the results derived from EPR spectra (Fig. 2) which consist of two distinct signals: one sharp signal ($g=2.009$ and $\Delta H=16$ G at 290 K) undoubtedly from the VT radical

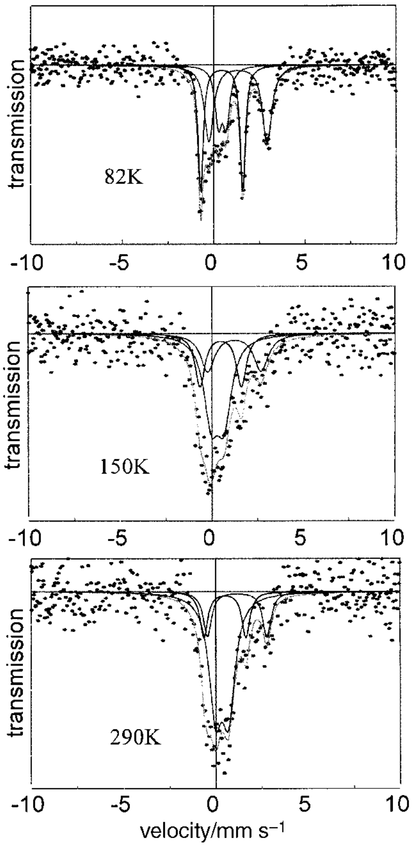


Fig. 4 ^{57}Fe Mössbauer spectra of **5H·(BF$_4$)$_4$**.

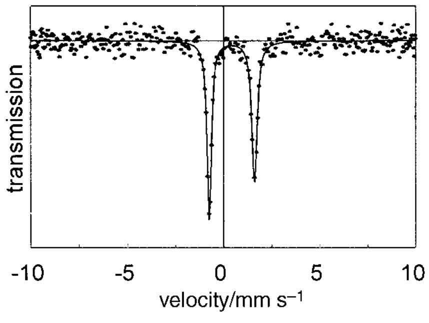
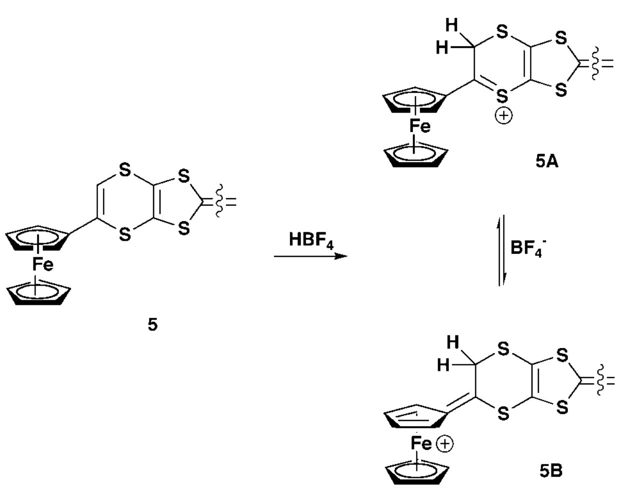
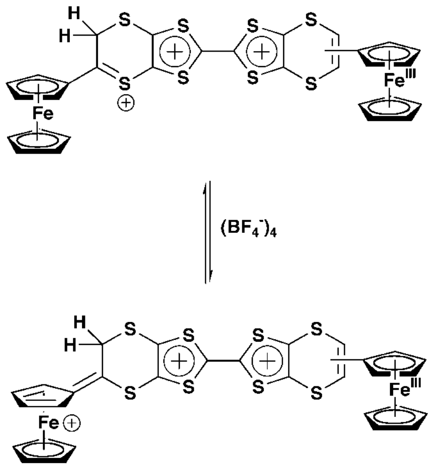


Fig. 3 ^{57}Fe Mössbauer spectrum of **5·(I$_3$)** at 82 K.



Scheme 3



Scheme 4 Proposed structure of **5H·(BF$_4$)$_4$** at 150 K.

cation as in the polyiodide compound and the other broad signal ($g = 2.006$ and $\Delta H = 400$ G at 290 K) possibly from paramagnetic transition metals.[5] The same pattern is obtained at 82 K, too, except for the abrupt intensity decrease of the broad signal. It is indicative of a decrease of population of paramagnetic ions in the BF$_4^-$ salt with decreasing temperature, even though the possibility of strong antiferromagnetic coupling at low temperature can not be ruled out completely. The ratio of Fe(II) and Fe(III) in the Mössbauer spectrum measured at 150 K is almost unity. With these data, we propose the structure of **5H·(BF$_4$)$_4$** at 150 K (Scheme 4): in which, due to protonation, the extended π-electron system of the VT moiety would be degraded into the TTF system which can accommodate two BF$_4^-$ ions and form dicationic TTF.[16] In this case the VT unit cannot serve any more as an effective bridge for electronic communication between the two ferrocenes because of the breakage of the extended π-electron system by the protonation. This will affect the electrical conductivity of this salt.

Electrical conductivity

The electrical conductivities of compressed pellets of **5·(I$_3$)** and **5H·(BF$_4$)$_4$** were about 7×10^{-3} S cm^{-1} at room temperature. They are very close to that of the DDQ salt of **IV** (1×10^{-3} S cm^{-1})[4] which is mainly due to the presence of the tetrathiafulvalenium ion, but less than that of VT(I$_3$)$_{0.4}$ (~ 160 S cm^{-1})[7] and VT(PF$_6$)$_{0.5}$ single crystals (20 S cm^{-1}).[8] This can be attributed to the fact that ferrocenyl groups on the peripheries of the molecule may prevent close contact of the VT unit in **5·(I$_3$)**. On the other hand, the extended π-electron system of the VT moiety is destroyed in **5H·(BF$_4$)$_4$** and therefore it does not serve as an effective bridge for intramolecular electron transfer in the mixed-valence state.

Acknowledgements

The author (D. Y. Noh) wishes to acknowledge the financial support of the Korea Research Foundation in the program year of 1997. The work in Bangor was funded by the EPSRC.

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