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Electrochemical and NMR spectroscopic studies of selenium- and tellurium-substituted ferrocenes II: Diferrocenyl chalcogenides, Fc_2E, diferrocenyl dichalcogenides, Fc_2E_2, and bis(ferrocenylchalcogeno)-alkanes, $FcE(CH_2)_nE'Fc$ ($E, E' = Se$: $n = 1, 2, 3$; $E, E' = Te$: $n = 1, 3$; $E = Se, E' = Te$: $n = 3$; $Fc = [Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)]$)

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Abstract

1,3-Bis(ferrocenylchalcogeno)propanes, $FcE(CH_2)_3E'Fc$ ($E, E' = Se, Te$), and 1,2-bis(ferrocenylseleno)ethane, $FcSe(CH_2)_2SeFc$ have been prepared, characterised, and included in a spectroscopic and electrochemical study of a series of compounds containing two ferrocenes linked by a chalcogen-containing bridge. Cyclic and differential pulse voltammetry show that there is electronic communication between the two ferrocene units when the bridge is short (as in Fc_2E), but that the interaction rapidly becomes weaker with increasing Fe···Fe distance, and is undetectable for the ethane and propane derivatives. ^{77}Se and ^{125}Te NMR spectroscopic measurements reveal that the ^{77}Se chemical shift of Fc_2Se_2 is anomalously high, which correlates with the long wavelength of its lowest energy electronic absorption.

Keywords: Ferrocene; Selenium; Tellurium; Electrochemistry; NMR spectroscopy

1. Introduction

From the 1970s onwards, several series of biferrocenes [1], bridged diferrocenes [2,3] and poly(vinylferrocene)s [4] have been synthesized. Much of the interest in these systems comprising more than one ferrocenyl unit has focused on the interactions between the iron centres, and their relevance to the study of multiple electron-transfer reactions. Electrochemical techniques have been widely used to investigate the iron–iron interactions, as one can use the most chemically stable member of a redox series; also the equipment and the experiment are relatively simple [5]. The separation, ΔE, between the oxidation potentials of the ferrocenyl units provides a measurement of charge interaction between the two reaction sites. This can be affected by many factors, such as bridge atoms, bridge type, etc.

Compared to studies of ferrocenes linked by carbon and silicon atom bridges, those of compounds where the bridge contains chalcogen atoms (especially Se and Te) have previously been quite unsystematic. We have now prepared and investigated several series of selenium- and tellurium-bridged diferrocenes, comprising diferrocenyl chalcogenides, diferrocenyl dichalcogenides, and bis(ferrocenylchalcogeno)alkanes, and have observed the effect of bridge length upon the electrochemistry. Also, the ^{77}Se or ^{125}Te NMR spectrum of each compound has been recorded, in order to study the $\delta(^{125}Te)/\delta(^{77}Se)$ ratios and to allow comparison with the data for ferrocenyl alkyl chalcogenides.

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2. Results and discussion

2.1. Synthesis and characterisation of bis(ferrocenylchalcogeno)alkanes

Bis(ferrocenylchalcogeno)methanes were originally prepared by Herberhold and Leitner [6]. We have now synthesised bis(ferrocenylchalcogeno)alkanes having a longer hydrocarbon chain by a similar method, as shown in Eq. (1). Reduction of the diferrocenyl dichalcogenide by sodium borohydride in ethanol was followed by addition of a α,ω-dihaloalkane. After column chromatography the product was generally isolated as an orange-yellow (E = Se) or orange-red (E = Te) solid in good yield. Care needs to be taken, however, to avoid the use of a large excess of reducing agent, which can result in almost exclusive formation of the monoferrocenyl compounds FcER (R = Et or Pr).

$$\begin{aligned}&\mathrm{FcEEFc}\xrightarrow[\text{ethanol}]{\mathrm{NaBH_4}}\mathrm{FcE^-}\xrightarrow[\text{reflux}]{\mathrm{X(CH_2)}_n\mathrm{X}}\mathrm{FcE(CH_2)}_n\mathrm{EFc}\\ &n = 1,3 : \mathrm{E} = \mathrm{Se, Te; X = I}\\ &n = 2 : \mathrm{E} = \mathrm{Se\ only; X = Br}\end{aligned}\qquad(1)$$

There are some differences between the behaviour of selenium and tellurium in this system, which are presumably a reflection of the greater nucleophilicity of the ferrocenyltellurolate anion. If the reaction of $\mathrm{FcE^-}$ (E = Se, Te) with $\mathrm{I(CH_2)_3I}$ is carried out under reflux, $\mathrm{FcE(CH_2)_3EFc}$ is obtained as the sole product in each case. At room temperature, however, a second compound can be isolated when E = Se, which has been identified as $\mathrm{FcSe(CH_2)_3I}$ (Eq. (2)). In this nucleophilic substitution reaction, the first $\mathrm{FcSe^-}$ anion rapidly replaces the leaving group $\mathrm{I^-}$, but the second step is much slower. The mechanism is shown in Scheme 1. The availability of $\mathrm{FcSe(CH_2)_3I}$ allowed us to prepare the mixed Se/Te compound $\mathrm{FcSe(CH_2)_3TeFc}$, as shown in Eq. (3). Dibromoalkanes are generally less reactive than their iodine analogues, and it is possible to isolate both mono-substituted derivatives $\mathrm{FcE(CH_2)_3Br}$ (E = Se, Te) from the reaction of $\mathrm{Br(CH_2)_3Br}$ with $\mathrm{FcE^-}$ [7].

$$\mathrm{FcSe^-}\xrightarrow[\text{ethanol, room temperature}]{\mathrm{I(CH_2)_3I}}\mathrm{FcSe(CH_2)_3I + FcSe(CH_2)_3SeFc}\qquad(2)$$

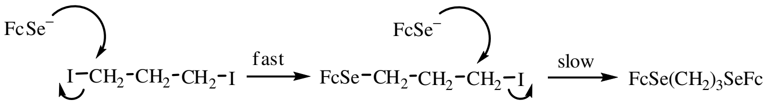
$$\mathrm{FcTeTeFc}\xrightarrow[\text{ethanol}]{\mathrm{NaBH_4}}\mathrm{FcTe^-}\xrightarrow[\text{reflux}]{\mathrm{FcSe(CH_2)_3I}}\mathrm{FcTe(CH_2)_3SeFc}\qquad(3)$$

The reactions with $\mathrm{I(CH_2)_2I}$ led to recovery of the diferrocenyl dichalcogenide, seemingly because the iodide ion acts as a dehalogenating agent in an 1,2-elimination reaction (Scheme 2) [8]. Changing to the dibromide $\mathrm{Br(CH_2)_2Br}$ allowed the isolation of the selenide $\mathrm{FcSe(CH_2)_2SeFc}$, but this compound could not be obtained pure and was always contaminated by traces of $\mathrm{Fc_2Se_2}$. The tellurium analogue remains elusive.

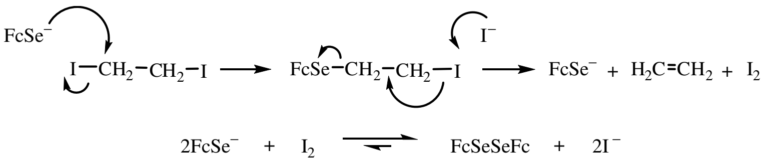
The ^{1}H and ^{13}C NMR spectra are summarised in Table 1 (including, for completeness, our data for $\mathrm{Fc_2E}$, $\mathrm{Fc_2E_2}$ and $\mathrm{FcECH_2EFc}$, which are generally the same as those previously reported by other authors). The same general trends were observed as have already been noted for ferrocenyl alkyl chalcogenides [9] and $\mathrm{RE(CH_2)}_n\mathrm{ER}$ (R = Me, Ph; n = 1, 2, 3; E = Se, Te) [10,11]. Except in $\mathrm{Fc_2E_2}$, the chemical shifts of H-3 and H-4 are similar to that of the hydrogens in the unsubstituted cyclopentadienyl ring; H-2 and H-5 resonate further downfield. The coupling constants $^{2}J_{\mathrm{E-H}}$ could only be measured for the compounds $\mathrm{FcECH_2EFc}$, where they were approximately half as great as in $\mathrm{MeECH_2EMe}$.

In the ^{13}C NMR spectra, the 'heavy-atom effect' generally results in the ^{13}C shifts of the *ipso*-carbon atoms bound to tellurium being shifted upfield with respect to their selenium analogues. The compounds $\mathrm{FcE(CH_2)_3EFc}$ represent an exception, however: here the chemical shifts of $\mathrm{ECH_2}$ are 29.9 ppm (E = Se) and 34.1 ppm (E = Te). Carbon–chalcogen coupling was resolved in a number of cases. As expected, coupling between C-1 and ^{125}Te is the strongest.

The electronic absorption spectra of ferrocene and its derivatives are well understood [12,13]. There are usually two characteristic bands in the UV/Vis region: one absorption around 440 nm, attributed to the $^{1}\mathrm{E}_{1g} \leftarrow {}^{1}\mathrm{A}_{1g}$ transition, and another one around 325 nm with the assignment $^{1}\mathrm{E}_{2g} \leftarrow {}^{1}\mathrm{A}_{1g}$. UV/Vis data are summarised in



Scheme 1.



Scheme 2.

Table 1
^1H and ^{13}C NMR data (δ/ppm; J/Hz) for diferrocenyl chalcogenides, diferrocenyl dichalcogenides and bis(ferrocenylchalcogeno)alkanes in $CDCl_3$ solution

Compound	C_5H_5		C_5H_4 (3,4)[a]		C_5H_4 (2,5)[a]		C_5H_4 (1)		–ECH_2–		–$CH_2CH_2CH_2$–	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C ($^2J_{E–C}$)	^1H	^{13}C ($^1J_{E–C}$)	^1H ($^2J_{E–H}$)	^{13}C ($^1J_{E–C}$)	^1H	^{13}C
Fc_2Se	4.11	69.7	4.08	69.8	4.24	74.6	–	69.7	–	–	–	–
FcSeSeFc	4.08	69.6	4.22	71.0	4.26	75.8	–	69.8	–	–	–	–
$FcSeCH_2SeFc$	4.10	69.7	4.14	70.2	4.27	75.5	–	72.1 (111)	3.61 (7.8)	24.4 (86)	–	–
$FcSeCH_2CH_2SeFc$	4.09	69.7	4.11	70.1	4.19	75.7	–	73.6	2.71	29.6 (64)	–	–
$FcSe(CH_2)_3SeFc$	4.10	68.3	4.11	68.7	4.19	74.3	–	69.2	2.54[b]	29.9	1.78[b]	28.0
Fc_2Te	4.07	69.6	4.10	71.3	4.29	78.9 (44)	–	49.2 (159)	–	–	–	–
FcTeTeFc	4.09	69.7	4.20	71.9	4.29	79.4	–	41.4	–	–	–	–
$FcTeCH_2TeFc$	4.07	69.5	4.17	71.8	4.31	79.7	–	48.1	3.40 (12.5)	Not observed	–	–
$FcTe(CH_2)_3TeFc$	4.07	69.7	4.13	71.6	4.24	79.8 (43)	–	43.7 (304)	2.53[b]	34.1 (156)	1.95[b]	11.2
$FcSe(CH_2)_3TeFc$	4.10	70.6	4.13	71.6	4.24	79.8	–	69.7	2.54[b]	32.7	1.87[b]	8.5
	4.07	69.7	4.10	70.0	4.18	75.7		43.6	2.51[b]	31.7		

[a] The ^1H resonances of $H_{3,4}$ and $H_{2,5}$ (which constitute an AA′BB′ spin system) appear as virtual triplets.

[b] The ^1H resonances of the –$CH_2CH_2CH_2$– group are multiplets.

Table 2
UV/Vis absorption of diferrocenyl chalcogenides, diferrocenyl dichalcogenides and bis(ferrocenylchalcogeno)alkanes in MeCN solution

	λ_1 (nm)	ε_1 (dm^3 mol^{-1} cm^{-1})	λ_2 (nm)	ε_2 (dm^3 mol^{-1} cm^{-1})
Fc_2Se	–	–	440	265
FcSeSeFc	370	800	440	555
$FcSeCH_2SeFc$	–	–	440	280
$FcSeCH_2CH_2SeFc$	–	–	440	280
$FcSe(CH_2)_3SeFc$	–	–	440	230
Fc_2Te	–	–	450	190
FcTeTeFc	395	2130	455	1500
$FcTeCH_2TeFc$	330	1910	455	320
$FcTe(CH_2)_3TeFc$	–	–	445	250
$FcSe(CH_2)_3TeFc$	–	–	445	300

Table 2. In all of the ferrocenyl selenides studied, the low wavelength band could not be resolved, and only the absorption at 440 nm was observed. In Fc_2Se_2 there is a second band around 370 nm, which can be attributed to the Se-localized n → σ^*(Se–Se) transition. It occurs at a slightly higher wavelength than is typical for organic diselenides [14,15]. It has been postulated that torsional distortion from 90° of the dihedral angle about the C_2 molecular symmetry axis causes a bathochromic shift of the lowest energy electronic absorption of diselenides, R_2Se_2 [16,17]. The dihedral angle in Fc_2Se_2 is −88.7(4)° [18], much closer to 90° than the corresponding value of 97.1(3.0)° in diphenyl diselenide [19]. This should result in a smaller red shift, so we speculate that the ferrocenyl group also affects the HOMO or LUMO energy of the Se–Se bond. In the ferrocenyl tellurides, the band due to the $^1E_{1g} \leftarrow {}^1A_{1g}$ transition of ferrocene is bathochromically shifted by ca. 10 nm, which may indicate that tellurium is able to act as a better π-donor than selenium in this type of compound. Unfortunately it was not possible to resolve two maxima in the spectrum of $FcSe(CH_2)_3TeFc$, which would have confirmed this. In Fc_2Te_2, the band due to the Te-localized n → σ^*(Te–Te) transition occurs at 390 nm, which is quite similar to the λ_{max} of organic ditellurides such as Ph_2Te_2 (406 nm) [20]. The dihedral angles in Fc_2Te_2 and Ph_2Te_2 are also similar (−86.1(4)° [21] and 88.5° [22], respectively). Uniquely amongst the bis(ferrocenylchalcogeno)alkanes, in $FcTeCH_2TeFc$ there is also a distinct low wavelength absorption at 330 nm, which might be assigned to the $^1E_{2g} \leftarrow {}^1A_{1g}$ transition of the ferrocenyl group.

2.2. ^{77}Se and ^{125}Te NMR spectroscopy

The ^{77}Se NMR and ^{125}Te NMR spectroscopy data are summarised in Table 3. For these heavy nuclei the paramagnetic term is expected to be the dominant contributor to the chemical shift [23], and σ^{para} is related to several factors as shown in Eq. (4). In the dichalcogenides, the asymmetry of the molecules brings about considerable deviations from spherical symmetry of the electron cloud, and results in an increase in ΔE^{-1} and $\sum Q$. The chemical

Table 3
^{77}Se and ^{125}Te NMR data for diferrocenyl chalcogenides, diferrocenyl dichalcogenides and bis(ferrocenylchalcogeno)alkanes in $CDCl_3$ solution

Compound	$\delta(^{77}Se)$ (ppm)		$\delta(^{125}Te)$ (ppm)		$\delta(^{125}Te)/\delta(^{77}Se)$
	Calculated	Observed	Calculated	Observed	
Fc_2E		210		347	1.65
Fc_2E_2		484		381	0.79
$FcECH_2EFc$	222	252	386	413	1.64
$FcE(CH_2)_2EFc$	225	232		–	
$FcE(CH_2)_3EFc$	179	185	278	295	1.59
$FcSe(CH_2)_3TeFc$		188		299	1.59

shift of a dichalcogenide is thus always higher than that of the corresponding chalcogenide. Some diselenides, however, have exceptionally high ^{77}Se chemical shifts: Fc_2Se_2 and Ph_2Se_2 are examples. This is associated with the relatively high wavelength of the $n \rightarrow \sigma^*$(Se–Se) transition in these compounds (vide supra), and thus with a smaller excitation energy ΔE. A similar phenomenon has been observed in the selones [24], where ^{77}Se chemical shifts correlated linearly with the energy of the $n \rightarrow \pi^*$ transition.

$$\sigma^{\text{para}} \propto -[r^{-3}]_{\text{np}} \sum Q/\Delta E \qquad (4)$$

where r is the radius of the np orbital; Q, the imbalance of charge in the valence shells; and ΔE is the effective excitation energy.

The ratio $\delta(^{125}\text{Te})/\delta(^{77}\text{Se})$ is generally constant for chemically similar compounds, and the values obtained here are in accordance with previous theoretical and empirical investigations [23]. Notably, the value of 1.59 for $FcE(CH_2)_3E'Fc$ is the same as that for ferrocenyl alkyl chalcogenides [9]. The ratio is slightly greater (1.64) for the compounds Fc_2E and $FcECH_2EFc$ in which the bridge between the two ferrocenes is shorter. In $FcSe(CH_2)_3TeFc$, it was possible to observe coupling between the two different chalcogen nuclei, with the coupling constant $^4J(^{77}\text{Se}–^{125}\text{Te}) = 11.72$ Hz.

It has been shown that the ^{77}Se chemical shifts of unsymmetrical selenides RR′Se can be predicted with reasonable accuracy if those of the corresponding symmetrical selenides are known, since the shifts associated with R and R′ are additive [23]. The chemical shift of Fc_2Se is 210 ppm (N.B. the value previously reported in Ref. [9] was in error). The contribution of each ferrocenyl group (δ(Fc)) is thus 105 ppm. Using published data for $MeSe(CH_2)_n$-SeMe [10], and knowing from the Me_2Se reference that $\delta(\text{Me}) = 0$, gives $\delta((CH_2)_n) = 117$ ($n = 1$), 120 ppm ($n = 2$) and 74 ppm ($n \geqslant 3$). Changes more remote than the γ-carbon atom have a negligible effect on $\delta(^{77}\text{Se})$. The chemical shifts calculated on this basis for the compounds $FcSe(CH_2)_nSeFc$ showed a good match to the observed data. A similar procedure can be adopted for the analogous tellurides. From $MeTe(CH_2)_3TeMe$ (104 ppm) [10], one can assign a contribution of 104 ppm to a $(CH_2)_n$ ($n \geqslant 3$) group, knowing $\delta(\text{Me}) = 0$. Using $\delta(\text{Fc}) = 174$ leads to a predicted chemical shift for $FcTe(CH_2)_3TeFc$ of 278 ppm; the observed value is 295 ppm (Table 2). The agreement between calculated and observed values is worst for the methylene derivatives $FcECH_2EFc$. This is to be expected, as the calculations are based on the substituent CH_2SeMe, rather than CH_2SeFc.

2.3. Electrochemistry

Cyclic and differential pulse voltammetries were used to investigate the reversibility of the ferrocenium-ferrocene redox couple. The half wave potentials ($E_{1/2}$) determined by cyclic voltammetry, and the peak potentials (E_p) measured by differential pulse voltammetry, are listed in Table 4. The cyclic voltammograms of diferrocenyl diselenide and the bis(ferrocenylseleno)alkanes are shown in Fig. 1.

The $E_{1/2}/E_p$ values of the selenium-containing compounds are all more positive than that of ferrocene itself. This can be attributed to the electronegative selenium atom, which is bonded directly to the Cp ring, causing the oxidation to be more difficult than that of unsubstituted ferrocene [9,25]. The cyclic voltammogram (CV) of diferrocenyl selenide showed two clearly reversible one-electron oxidation processes, with $E_{1/2}$ values of 26 mV and 234 mV, indicating that the ferrocenyl moieties are not acting independently, $\Delta E = 208$ mV. The cyclic voltammogram of diferrocenyl diselenide was similar, showing two clearly reversible waves with $E_{1/2}$ values of 84 mV and 245 mV, $\Delta E = 161$ mV. These data are in accord with the results of Shu et al., who reported $\Delta E = 220$ mV and 140 mV, respectively, for these compounds [3]. With increased distance between the ferrocenyl moieties, the interaction between them decreased quickly: $\Delta E = 111$ mV for $FcSeCH_2SeFc$. Only one well defined quasi-reversible wave was observed for $FcSe(CH_2)_2SeFc$ ($E_{1/2} = 72$ mV)

Table 4
Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) results for diferrocenyl chalcogenides, diferrocenyl dichalcogenides and bis(ferrocenylchalcogeno)alkanes (mV, relative to $FcH/[FcH]^+$)

	E_1		E_2		E_3	
	CV	DPV	CV	DPV	CV	DPV
	$E_{1/2}$ ($\lvert E_{pa} - E_{pc}\rvert$)	E_p	$E_{1/2}$ ($\lvert E_{pa} - E_{pc}\rvert$)	E_p	$E_{1/2}$ ($\lvert E_{pa} - E_{pc}\rvert$)	E_p
Fc_2Se	26 (65)	35	234 (60)	236	–	–
Fc_2Se_2	84 (73)	96	245 (83)	252	–	–
$FcSeCH_2SeFc$	41 (66)	40	145 (77)	151	–	–
$FcSe(CH_2)_2SeFc$	72 (130)	96	–	–	–	–
$FcSe(CH_2)_3SeFc$	48 (102)	50	–	–	–	–
Fc_2Te	6 (65)	5	221 (52)	237	376 (88)	402
Fc_2Te_2	35 (93)	60	172 (69)	186	Unresolved	312
$FcTeCH_2TeFc$	27 (56)	35	126 (70)	130	364 (99)	362
$FcTe(CH_2)_3TeFc$	−11 (92)	−26	–	–	410 (268)	393
$FcSe(CH_2)_3TeFc$	31 (71)	38	–	–	352 (95)	357

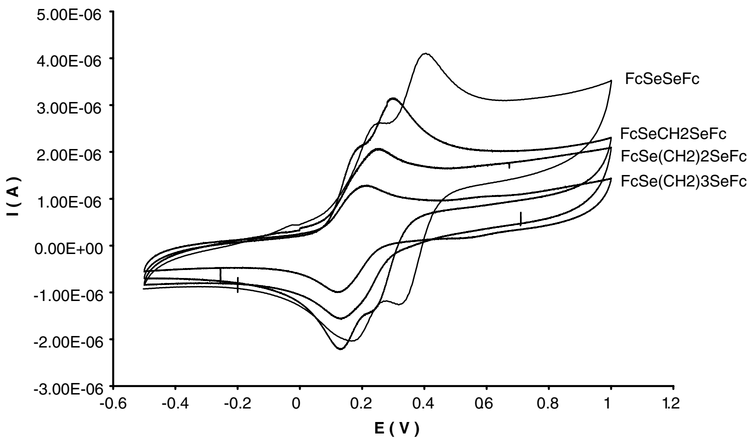


Fig. 1. Cyclic voltammograms of $FcSe(CH_2)_nSeFc$ ($n = 0, 1, 2, 3$) in dry acetonitrile, 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of $100\ mV\ s^{-1}$.

and $FcSe(CH_2)_3SeFc$ ($E_{1/2} = 48$ mV), indicating that the ferrocenyl moieties are acting independently in terms of their electrochemistry.

There are two possible mechanisms for communication between ferrocenes: "through space" or "through bond". Comparison between the behaviour of FcSeSeFc and that of $FcCH_2CH_2Fc$ shows the importance of the nature of the bridging atoms (particularly those bound directly to the cyclopentadienyl rings): the cyclic voltammogram of FcSeSeFc shows two waves, whereas for $FcCH_2CH_2Fc$ there is only one [3]. It is therefore generally accepted that the through bond mechanism is operating in these systems. In the series of bis(ferrocenylseleno)alkanes, $FcSe(CH_2)_n$-SeFc, as the length of the hydrocarbon chain increases, the Fe···Fe through bond distance becomes greater, and the difference between the two half wave potentials decreases, until it is undetectable when $n \geqslant 2$.

The electrochemical data obtained for the diferrocenyl tellurides are more complicated. The cyclic voltammogram of diferrocenyl telluride showed two reversible waves, with $E_{1/2}$ values of 6 mV and 221 mV ($\Delta E = 215$ mV), and one quasi-reversible wave with an $E_{1/2}$ value of 376 mV. With the benefit of the information obtained for ferrocenyl alkyl tellurides [9], we can easily attribute the third wave to the tellurium acting as a redox centre. Similarly there exist three waves for diferrocenyl ditelluride, with $E_{1/2}$ values of 35 mV and 172 mV for the ferrocenyl moieties, $\Delta E = 137$ mV. The interaction between the iron centres in Fc_2Te_2 is weaker than in Fc_2Se_2, in accordance with the difference in Fe···Fe through bond distance (10.213 Å for Fc_2Se_2, 11.01 Å for Fc_2Te_2) [18,21]. The communication between the ferrocenyl groups decreases in $FcTeCH_2TeFc$, with $\Delta E = 99$ mV, 12 mV less than in $FcSeCH_2SeFc$. Based on the behaviour of its Se analogue, $FeTe(CH_2)_3TeFc$ should exhibit no interaction between the iron centres; as expected the cyclic voltammogram contains only one ferrocene-based wave. This occurs, however, at unusually low potential ($E_{1/2} = -11$ mV); the tellurium-based wave with $E_{1/2} = 410$ mV also has quite a large separation between cathodic and anodic peaks ($|E_{pa} - E_{pc}| = 268$ mV). We have no explanation for these features at present. More complicated electrochemical behaviour might have been predicted for $FcSe(CH_2)_3TeFc$, but it appears that the oxidation potentials of the two chemically different ferrocene units are too close for the resolution of separate features in the voltammograms. The relative intensity of the tellurium-based redox process ($E_{1/2} = 352$ mV) is of course approximately half that exhibited by the compounds containing two tellurium atoms.

3. Experimental

All reactions were performed using standard Schlenk techniques and pre-dried solvents under an atmosphere of dinitrogen. ^{1}H and ^{13}C NMR spectra: Bruker AC400; tetramethylsilane as internal standard. ^{77}Se and ^{125}Te NMR spectra: Bruker WM250; dimethyl selenide or dimethyl telluride as external standard. IR spectra: Perkin–Elmer 1725X. UV/Vis spectra: Perkin–Elmer UV/Vis/NIR Lambda 9. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using electron impact (EI) or fast atom bombardment (FAB); m/z values are reported to the nearest integer; assignments are based on isotopomers containing ^{1}H, ^{12}C, ^{56}Fe, and ^{80}Se or ^{130}Te; expected isotope distribution patterns were observed. CV and differential pulse voltammetry (DPV): Autolab PGSTAT30 potentiostat system; Pt working and auxiliary electrodes; Ag/Ag^{+} (0.01 M $AgNO_3$ in CH_3CN) as reference electrode; 0.1 M $[NBu_4][PF_6]$ in CH_3CN as supporting electrolyte; scan rates $100\ mV\ s^{-1}$ (CV), $72\ mV\ s^{-1}$ (DPV). Elemental analyses were performed by Butterworth Laboratories Ltd., Teddington, Middlesex, UK.

Fc_2E_2 (E = Se, Te) were prepared from $[Fe(\eta^5\text{-}C_5H_5)_2]$ (FcH) via lithiation in THF with 0.9 equivalents of Li^tBu, treatment with selenium or tellurium, and air oxidation, in a minor modification of the literature procedure [6]. The same authors' methods were used for the synthesis of Fc_2E and $FcECH_2EFc$ (E = Se, Te).

3.1. $FcSe(CH_2)_3SeFc$ and $FcSe(CH_2)_3I$

Fc_2Se_2 (0.527 g, 1 mmol) was dissolved in EtOH (50 ml), and the solution cooled to 0 °C. $NaBH_4$ (0.151 g, 4 mmol) was then added. After warming to room temperature and stirring for 2 h, the mixture became homogeneous. An ethanol solution of $I(CH_2)_3I$ (3.1 ml, 4% v/v, 1 mmol) was added, and the mixture left to stir overnight. The solvent was removed by evaporation under reduced pressure. The residue was treated with water (25 ml) and extracted with CH_2Cl_2 (3×25 ml). The extract was dried over $MgSO_4$ and evaporated to dryness, then subjected to column chromatography on SiO_2. Elution with hexane/dichloromethane (3:1) produced two bands: the first contained $FcSe(CH_2)_3I$, an orange-yellow oil, yield 0.065 g (30%); the second contained $FcSe(CH_2)_3SeFc$, an orange-yellow solid, yield 0.128 g (45%). Carrying out this reaction under reflux led to the exclusive formation of $FcSe(CH_2)_3SeFc$, yield 70%.

3.1.1. $FcSe(CH_2)_3SeFc$

$C_{23}H_{24}Fe_2Se_2$: calcd. C 48.46, H 4.24; found: C 47.18, H 4.11. FAB MS: 572 (M^+, 100%), 265 ($FcSe^+$, 96%), 226 ($FcCH_2CH{=}CH_2^+$, 67%). ^1H, ^{13}C, ^{77}Se NMR: see Tables 1 and 3.

3.1.2. $FcSe(CH_2)_3I$

FAB MS: 434 (M^+, 100%), 265 ($FcSe^+$, 20%). ^1H NMR: 4.12 (C_5H_5, s, 5H), 4.14 (C_5H_4, H_{3+4}, m, 2H), 4.24 (C_5H_4, H_{2+5}, m, 2H), 3.17 (ICH_2, t, 2H, $^3J_{H-H} = 8.8$ Hz), 2.57 ($SeCH_2$, t, 2H, $^3J_{H-H} = 8.8$ Hz), 1.99 ($CH_2CH_2CH_2$, m, 2H). ^{13}C NMR: 75.2 (C_5H_4, C_{2+5}), 70.3 (C_5H_4, C_{3+4}), 70.2 (C_1), 69.8 (C_5H_5), 34.0 (CH_2I), 30.1 ($SeCH_2$, $^1J_{Se-C} = 63.6$ Hz), 6.7 ($CH_2CH_2CH_2$). ^{77}Se NMR: 185.

3.2. $FcTe(CH_2)_3TeFc$

This compound was prepared by a similar method using Fc_2Te_2 and $I(CH_2)_3I$, yield 80%. $C_{23}H_{24}Fe_2Te_2$: calcd. C 41.40, H 3.62; found: C 41.26, H 3.41. FAB MS: 672 (M^+, 33%), 315 ($FcTe^+$, 100%). ^1H, ^{13}C, ^{125}Te NMR: see Tables 1 and 3.

3.3. $FcSe(CH_2)_3TeFc$

This compound was prepared by a similar method using Fc_2Te_2 and $FcSe(CH_2)_3I$, yield 90%. $C_{23}H_{24}Fe_2SeTe$: calcd. C 44.65, H 3.91; found: C 44.58, H 3.81. FAB MS: 622 (M^+, 43%), 315 ($FcTe^+$, 85%), 265 ($FcSe^+$, 99%), 226 ($FcCH_2CH{=}CH_2^+$, 100%). ^1H, ^{13}C, ^{77}Se, ^{125}Te NMR: see Tables 1 and 3.

3.4. $FcSe(CH_2)_2SeFc$

This compound was prepared by a similar method using Fc_2Se_2 and $Br(CH_2)_2Br$, yield 72%. It could not be obtained completely free of Fc_2Se_2. EI MS: 558 (M^+). ^1H, ^{13}C, ^{77}Se NMR: see Tables 1 and 3.

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