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Mössbauer and electrochemical studies on some derivatives of 1,3-diselena- and 1,3-dithia-[3]ferrocenophanes

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Abstract

The oxidation potentials and the Mössbauer parameters are reported for ferrocene derivatives; the [3]ferrocenophanes $Fe(C_5H_4S)_2X$ (X = S, Se, Te, P(S)Ph) and $Fe(C_5H_4Se)_2X$ (X = Se, CH_2, CPh_2, PPh, P(S)Ph, SiPhMe), the spiro compounds $[Fe(C_5H_4Se)_2]X$ (X = Si, Sn) and the dichalcogenides $[(C_5H_5)Fe(C_5H_4X)]_2$ (X = S, Se).

Introduction

We have recently been interested in the synthetic and structural chemistry of [1]ferrocenophanes [1] and [3]ferrocenophanes [2]. Previously we have described the synthesis and some structural studies on some [3]ferrocenophanes in which atoms other than carbon are involved in the bridge [3,4]. We have now extended our study of this type of [3]ferrocenophane, and report here measurements of electrochemical properties and Mössbauer parameters for a representative selection of this type of compound.

Results and discussion

Reversible one-electron oxidation to the ferricenium cation is a characteristic reaction of ferrocene. Early qualitative experiments [5] revealed that the oxidation of ferrocene derivatives was related to the electronic character of the substituents attached to the cyclopentadienyl (Cp) rings. Thus electron-donating substituents facilitate oxidation and electron-withdrawing groups have the opposite effect. From our previous studies we have, for example, shown that for a [3]ferrocenophane involving a trimethylene bridge, the oxidation potential is decreased by 72 mV, i.e. 24 mV per methylene group [6].

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For the ferrocene derivatives studied in the present work, the half-wave potentials, $E_{1/2}$ vs. Ag/AgCl electrode, are listed in Table 1. The oxidation potential of the trithia-bridged [3]ferrocenophane is somewhat higher than ferrocene itself and hence the trithia bridge is a strong electron-withdrawing group. The increase in $E_{1/2}$ is 314 mV or approximately 105 mV per sulphur atom. The oxidation potential of the triselena[3]ferrocenophane shows that the triselena group is also electron-withdrawing with an average increase in $E_{1/2}$ of 76 mV per selenium atom.

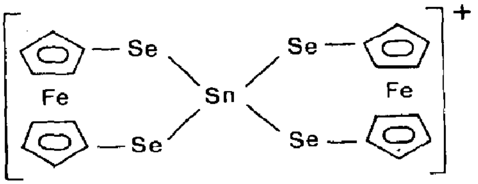
From these values it seems clear that the trithia bridge is much more electron withdrawing in character than the triselena bridge. Although it is difficult to estimate the overall interaction of the three atoms in the bridge, a rough approximation can be obtained from the ionisation potentials of the elements [7].

The data for compound **3** in Table 1 shows the effect of changing the central sulphur atom in the trithia bridge to a selenium atom. This results in a decrease in $E_{1/2}$ of 41 mV relative to the value of the parent trithia compound. Similarly for compound **4**, when a tellurium atom is introduced into the 2-position in the bridge, the $E_{1/2}$ is decreased by 152 mV relative to the parent trithia compound. This trend in the changes in $E_{1/2}$ is also in accord with the ionisation potential of these three elements.

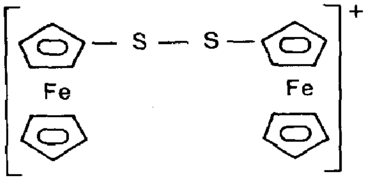
The introduction of a methylene group into the 2-position of the triselena compound has a similar though less pronounced effect upon the oxidation potential of the resultant molecule. Thus the electron-donating character of the methylene group is facilitating the oxidation of the molecule. However, substitution of the methylene hydrogens by phenyl groups, compound **6** in Table 1, has a surprising effect on the oxidation potential of the compound. In this molecule the phenyl groups are distant from the ferrocenyl moiety and yet they exert sufficient electron-withdrawing influence via the carbon and selenium atoms of the bridge to increase the $E_{1/2}$ value by 50 mV relative to the corresponding methylene compound. This increase may be compared with that observed when a phenyl group is directly bonded to the Cp ring; e.g. the value for phenylferrocene is 33 mV higher than that for ferrocene [8].

For those compounds which contain an organophosphorus group in the 2-position of the bridge, it is not surprising that the $E_{1/2}$ values indicate that the organophosphorus group is strongly electron withdrawing. As expected, the selenium compound containing phosphorus (V) (compound **8**) shows a higher oxidation potential than the corresponding compound containing phosphorus(III) (compound **7**). It is also noteworthy that the electron-withdrawing effect of a $>$P(S)Ph group in the 1,3-diselena[3]ferrocenophane is greater than that in the 1,3-dithia[3]ferrocenophane.

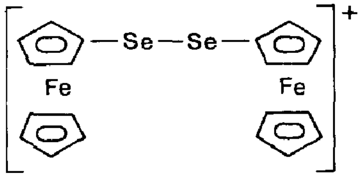
From the values of $E_{1/2}$ shown in Table 1, the electrode reaction of compounds **11**–**14** appears to involve two consecutive one-electron oxidation steps to give the corresponding mono- and then di-ferricenium cations. The results also show that it is significantly more difficult to remove the second electron than the first. This indicates an electronic interaction between the ferrocene and ferricenium units in the mono-cation through the side chain. For compound **12** decomposition was observed during the second oxidation process, and no evidence was obtained for the existence of the diferricenium cation which appears to be unstable under the reaction conditions used.



For compounds **13** and **14** the difference between the first and second oxidation potential is fairly large, and shows a considerable variation between the two compounds. This indicates the high electron-withdrawing strength of the radical **A** relative to that of the radical **B**.



(A)



(B)

For all of the ferrocene derivatives studied here, only the dominant electronic effects of the substituents are considered. The oxidation potential of the ferrocenyl moiety may however be influenced by other effects of the substituents; e.g. molecular deformations caused by steric requirements of the substituents, bond-shortening or ring-tilting of the Cp rings. The fine structural changes can be observed by this technique for those deviations which have small systematic changes in the construction of the molecule. This was observed in the case of the singly and multiply-bridged trimethylene[3]ferrocenophanes [6].

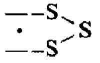
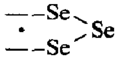
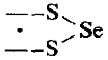
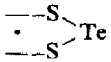
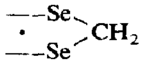
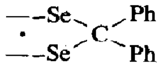
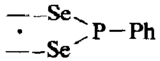
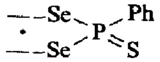
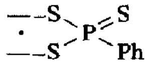
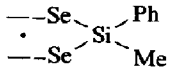
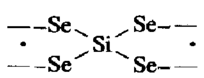
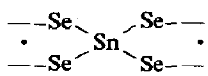
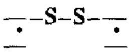
MO-LCAO SCF calculations related to ferrocene derivatives show that small but significant changes occur in the number of electrons in the *d* orbitals of the iron atom when the Cp ring is substituted by a $COCH_3$ or COOH group [9,10,11]. In each case the electron density is lowered in the $e_2(d_{x^2-y^2}, d_{xy})$ orbitals and is correspondingly increased in the $e_1(d_{xz}, d_{yz})$ orbitals. In the Mössbauer spectra this results in decreased quadrupole splittings (QS) but negligible changes in the isomer shifts (IS) [12]. A similar effect of the strongly electron-withdrawing carbonyl group is observed for the keto-derivatives of the tri- and tetra-methylene-bridged ferrocenes, in which a methylene group has been replaced by a carbonyl group [13]. Those compounds in which the carbonyl group is not coplanar with the Cp ring have proved to be exceptions to this generalisation [14]. Thus in some cases the fine details of the molecular structure can be derived from the Mössbauer parameters.

The ferrocene compounds in the present study are substituted by electron-withdrawing groups, as shown by the oxidation potentials (Table 1). Some of these compounds have been studied by the Mössbauer technique and the results are shown in Table 2. As expected, the QS values are lower than the QS of ferrocene. For those compounds which are directly comparable on the basis of structural similarity, namely compounds **1**, **3**, **4** and compounds **2**, **5**, **6**, in which the only differences are in the groups at the 2-position of the bridge, the QS values are in reasonable accord with the $E_{1/2}$ values, in that the higher the $E_{1/2}$ value the smaller the QS value. Unfortunately a more quantitative correlation between the QS and $E_{1/2}$ values for these compounds has not been found. Such a correlation has been found for some mono- and di-substituted ferrocenes [15].

The IS values for these [3]ferrocenes are very nearly the same as that for ferrocene itself, although compounds **4** and **7** have somewhat higher values. Although the change in IS values is very small it is noteworthy that ΔIS values are positive in most of the cases. This also supports the suggestion of rearrangements of the e_1 and e_2 molecular orbitals mentioned above.

Table 1

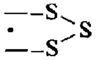
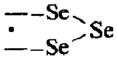
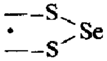
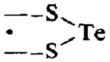
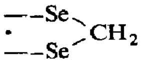
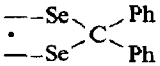
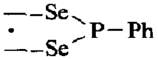
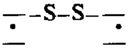
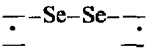
Oxidation potentials of some 1,3-dithia-, and 1,3-diselena-[3]ferrocenophanes (• = *ferrocenyl*)

No.	Compound	$E_{1/2}$ (mV)	$\Delta E^1_{1/2}$	$\Delta E^2_{1/2}$	$\Delta E^1_{1/2}/x$ [a]
1		774±2	314	–	104.7
2		688±2	228	–	76.0
3		733±1	273	−41	91.0
4		622±3	162	−152	54.0
5		646±2	186	−42	62.0
6		696±2	236	+8	78.7
7		777±2	317	+89	105.7
8		788±1	328	+100	109.3
9		831±1	371	+57	123.6
10		897±10	437	+209	145.7
11		480±2 701±3	20 241	– –	– –
12		592±7 –	152 –	– –	– –
13		578±2 726±4	118 266	– –	– –
14		646±5 708±7	186 248	– –	– –
15		460±5		–	–

[a] x = number of exocyclic bridge atoms, $\Delta E^1_{1/2} = E_{1/2}$ of the compound $- E_{1/2}$ of the ferrocene, $\Delta E^2_{1/2} = E_{1/2}$ of the compound $- E_{1/2}$ of the parent compound.

Table 2

Mössbauer parameters of some 1,3-dithia- and 1,3-diselena-[3]ferrocenophanes

No.	Compound	QS (mm/s)	ΔQS [a]	IS (mm/s)	ΔIS [a]
1		2.096(2)	−0.271	0.435(1)	0.003
2		2.158(5)	−0.209	0.442(3)	0.010
3		2.101(2)	−0.266	0.442(1)	0.010
4		2.183(5)	−0.184	0.449(3)	0.017
5		2.204(4)	−0.163	0.439(1)	0.007
6		2.130(5)	−0.237	0.425(6)	−0.007
7		2.244(3)	−0.123	0.454(2)	0.022
13		2.300(1)	−0.067	0.430(1)	−0.002
14		2.290(2)	−0.077	0.436(2)	0.004
15		2.367(2)	-	0.432(2)	-

[a] ΔQS and ΔIS related to the ferrocene.

Experimental

All the compounds used in this work have been reported previously [2,3,4].

Electrode potentials for the one-electron oxidation of these ferrocenes to their respective cations were measured by cyclic voltammetry [16]. A three-electrode cell was used in which the working and auxiliary electrodes were platinum and the reference electrode was Ag/AgCl (saturated). The solutions were tetrabutylammonium perchlorate (0.1 *M*) in a 1/1 mixture of acetonitrile and tetrahydrofuran. The oxidation potential of ferrocene was found to be 460 ± 5 mV (average value for 48 measurements). The oxidation potentials given in Table 1, except that for ferrocene, are the average values from three to five runs. The potentiostat was a Radelkis (Hungary) type OH-105. The measurements were made at a scan rate of 66 mV s^{-1}. Ferrocene and 1,1′,2,2′-bis(tetramethylene)-bridged ferrocene (308 mV) were used as internal standards to eliminate systematic errors.

The Mössbauer spectra were recorded at room temperature by means of a constant acceleration spectrometer using a ^{57}Co source in a chromium matrix. Metallic iron was used to calibrate the velocity scale. The Mössbauer parameters were evaluated by the least squares method. The Mössbauer parameters given in

Table 2 are the average values of three runs. The errors recorded are the standard deviations of the average of the results for each sample.

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