Syntheses and Physicochemical Properties of $Cu(BF_4)_2$ Complexes of Polythia[*n*]ferrocenophanes and the Corresponding Ferrocenium Cations

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1,5,9,13-Tetrathia[13]- and 1,5,8,12-tetrathia[12]-ferrocenophanes react with copper(II) tetrafluoroborate to give 1 : 1 complexes, while 1,5,9-trithia[9]ferrocenophane gives a 2 : 1 complex under the same conditions. Various physicochemical measurements showed that in these complexes the ferrocene nucleus was oxidized to ferrocenium and the copper atom incorporated in the thiamacrocycle was reduced to Cu^I. The quadrupole splitting values and magnetic moments of the sulphur-substituted ferrocenium cations and their copper(I) complexes showed a good correlation with the Prins parameter of low-symmetry perturbation (*x*) obtained from e.s.r. measurements.

There have been many reports of studies of heterobimetallic compounds from the viewpoint of their unique chemical character or certain stabilization by means of an unusual co-ordination mode.[1,2] Ferrocene derivatives having electron-donating substituents in the 1,1′ positions are useful organometallic ligands by which many heterobimetallic transition-metal complexes have been prepared[3] and used in catalytic reactions.[4,5] Ferrocenocrown ethers[6,7] and ferrocenothiacrown ethers (polythia[*n*]ferrocenophanes)[8] can also serve the same purpose. A silver(I) complex of a ferrocenocrown ether[9] and complexes of Cu^I, Ag^I, and Pd^{II} of ferrocenothiacrown ethers have been prepared.[10,11] We here report the synthesis and some properties of complexes obtained from the reaction of trithia- and tetrathia-[*n*]ferrocenophanes with $Cu(BF_4)_2$.

Table 1. Visible and i.r. spectral data of the complexes and the cations

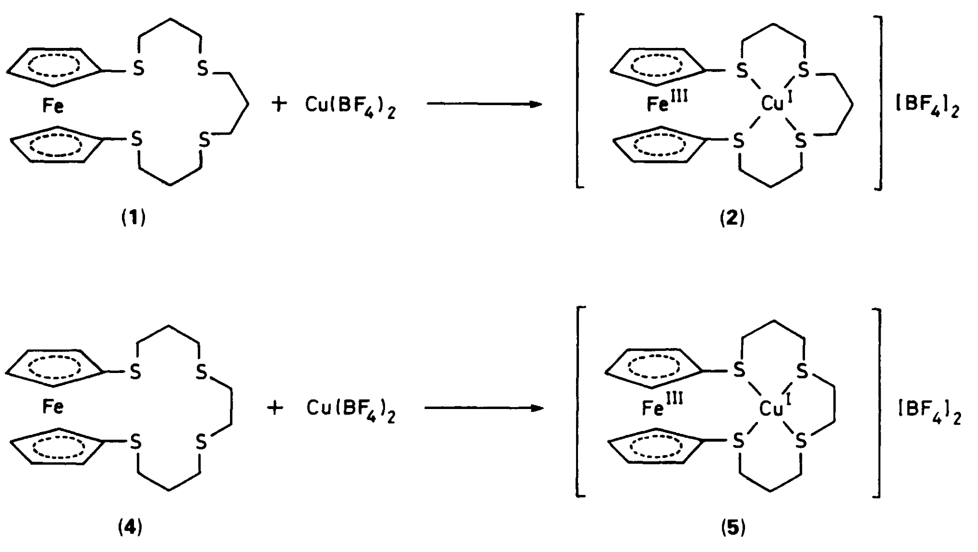
Compound	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	Out of plane bending vibration (cm^{-1})
(2)	872 (502), 760 (1 500), 436 (1 400)	848
(5)	850 (473), 760 (418), 448 (1 203)	844, 854
(8)	834 (980), 728 (930), 464 (2 830)	854, 820
(3)	856.5 (1 030), 760 (950), 456 (2 710)	846
(6)	863.5 (950), 760 (860), 453 (2 490)	844
(9)	850 (617), 742 (550), 466 (1 440)	850

The electronic spectra were measured in acetone [(2), (5), and (8)] or acetonitrile [(3), (6), and (9)] and the i.r. spectra in KBr disks.

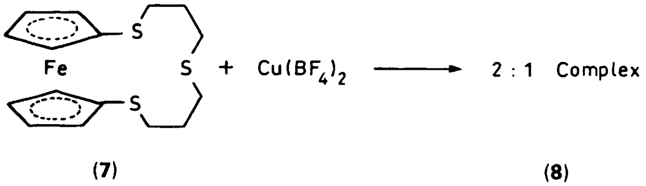
Results and Discussion

1,5,9,13-Tetrathia[13](1,1′)ferrocenophane (**1**) was treated with copper(II) tetrafluoroborate hydrate in ethanol not to give the copper(II)-containing complex but the corresponding copper-free ferrocenium cation (**3**) as black needles in good yield. The structure of (**3**) was identified by its i.r. and electronic spectra, superimposable upon those of an authentic sample prepared by oxidation of (**1**) with benzoquinone and boron trifluoride–diethylether. When a solution of complex (**1**) in nitromethane saturated with nitrogen was mixed with a solution of copper(II) tetrafluoroborate and acetic anhydride in nitromethane saturated with nitrogen and subsequently diluted with anhydrous ether fine black needles were isolated in 68% yield. They were confirmed by elemental analysis to be the 1 : 1 complex, (**2**), of (**1**) with $Cu(BF_4)_2$. In a similar manner, the 1 : 1 complex, (**5**), of 1,5,8,12-tetrathia[12](1,1′)ferrocenophane (**4**) with $Cu(BF_4)_2$ was obtained as black needles in 68% yield. In contrast, a similar procedure with 1,4,7,10-tetrathia[10](1,1′)- and 1,4,8,11-tetrathia[11](1,1′)-ferrocenophane afforded no corresponding stable complex. If the preparative procedure was done without nitrogen saturation of the solvent, the corresponding copper-free ferrocenium cations (**3**) and (**6**) were obtained instead of the copper-containing complexes (**2**) and (**5**). When (**2**) and (**5**) were recrystallized from acetonitrile the corresponding ferrocenium cations (**3**) and (**6**) were isolated as black plates in good yield, respectively. 1,5,9-Trithia[9](1,1′)ferrocenophane (**7**) was treated with copper(II) tetrafluoroborate hydrate in ethanol, followed by recrystallization from acetone–hexane to give the 2 : 1 complex (**8**) as black plates in 55% yield. The reaction of (**7**) with copper(II) tetrafluoroborate hydrate and acetic anhydride in nitrogen-saturated nitromethane gave the corresponding copper-free ferrocenium cation (**9**), which was also obtained on oxidation of the free ligand (**7**) with benzoquinone and $BF_3 \cdot OEt_2$ in benzene. In a similar reaction, 1,4,7-trithia[7]ferrocenophane gave no definite complex.

I.r. Spectra.—The i.r. spectrum of the 1 : 1 complex (**2**) was approximately similar to that of the corresponding copper-free cation (**3**), although different in detail. The absorption assigned to an unsymmetric metal–ligand stretching transition, which appeared at 486 cm^{-1} for (**1**), shifted to 416 cm^{-1} for (**2**) and 418 cm^{-1} for (**3**), respectively. Oxidation of ferrocene to a ferrocenium cation is reported[12] to cause a corresponding shift from 478 to 405—423 cm^{-1}. The C–H out of plane bending vibration, which is observed at 815 cm^{-1} for ferrocene, appears to be the most diagnostic for probing the oxidation state of a ferrocene nucleus.[13] For example, this absorption band for ferrocenium tri-iodide was found at 851 cm^{-1} (Δ 36 cm^{-1}). The free ligand (**1**) and its cation (**3**) showed the out of plane bending vibration at 816 and 846 cm^{-1}, respectively. The corresponding band of complex (**2**) was observed at 848 cm^{-1} indicating the presence of a ferrocenium component. For [0.0]ferrocenophane[14] and [2.2]ferrocenophane-1,13-diyne[15] in which the *d*



Scheme 1.



Scheme 2.

Table 2. Magnetic moments and e.s.r. parameters of the complexes [(2), (5), (8)] and the copper-free cations [(3), (6), (9)]

Compound	Magnetic moment $\mu_{eff.}$	E.s.r. parameters $g_{\parallel}$	$g_{\perp}$	k	x
(2)	2.61	—	—	—	—
(5)	2.39	3.36	1.81	0.80	0.47
(8)	2.10	2.89	1.93	0.84	0.27
(3)	2.09	2.93	1.91	0.77	0.32
(6)	1.81	2.73	1.96	0.91	0.21
(9)	2.13	2.93	1.91	0.77	0.32

electron on the iron atom of the ferrocene nucleus is delocalized on the time-scale of the i.r. measurement, the corresponding bands appeared at 835 and 842, and 831 cm^{-1}, respectively.[13] Therefore, the positive charge in complex (**2**) is suggested to be localized on the iron atom of the ferrocene nucleus, at least on the i.r. time-scale. In the i.r. spectrum of the 2:1 complex (**8**) the C–H out of plane bending vibration was observed at 820 and 854 cm^{-1}, while the free ligand (**7**) showed this band at 806 cm^{-1} and the corresponding cation (**9**) at 850 cm^{-1}. This suggests that (**8**) contains both neutral and oxidized ferrocene nuclei in the molecule.

Electronic Spectra.—The visible absorption pattern of the free ligands (**1**) and (**4**) was very similar to that of ferrocene itself although an increased absorption coefficient was observed. On the other hand, the corresponding ferrocenium cations (**3**) and (**6**) showed a rather different visible absorption to that of oxidized ferrocene.[16] For example, for (**6**) three absorptions were observed at 453 (2 490), 760 (860), and 863.5 nm (ε 950 dm^3 mol^{-1} cm^{-1}), while for ferrocenium tetrafluoroborate only one absorption appeared at 617 nm (log ε 2.53).[17] The latter absorption, which is suggested to be due to the allowed charge-transfer transition from the e_{1u} bonding ligand level to the hole in the e_{2g} level,[18] shifts to longer wavelength (*ca.* 700 nm) for the aryl-substituted ferrocenium cation,[19] probably because of conjugation between the phenyl group and a ferrocene nucleus. The two absorptions observed in the long-wavelength region are therefore possibly due to the charge-transfer transition, which may be attributed to the transition from the n$^+$ and n$^-$ levels to the hole of the e_{2g} level, because a large increase in energy of the cyclopentadienyl π orbitals (e_1' and e_1'') upon conjugation with the sulphur lone-pair level (n$_s$) was observed in photoelectron spectra of the sulphur-substituted ferrocenes.[20] This suggestion seems to be supported by the fact that the corresponding absorption is observed at 862 and 910 nm for the monocations of diferrocenyl selenide and n-butylferrocenyl selenide, respectively.[21]

The electronic spectra of complexes (**2**) and (**5**) greatly resembled those of the corresponding copper-free ferrocenium cations (**3**) and (**6**), respectively, throughout the u.v. and visible regions. This suggests that (**2**) and (**5**) contain ferrocenium components. No absorption was observed near 390 nm where a strong absorption characteristic of complexes of macrocyclic tetrathioethers with Cu^{II} was found.[22] These facts indicate that in (**2**) and (**5**) the ferrocene nucleus is oxidized to the ferrocenium cation and the copper atom incorporated in the thiamacrocycle moiety is reduced to the copper(I) state. This suggestion seems to be also supported by the fact when complexes (**2**) and (**5**) were recrystallized from acetonitrile they gave cations (**3**) and (**6**), respectively, since copper(I) has a strong affinity for acetonitrile.[23] The electronic spectrum of the 2:1 complex (**8**) is nearly superimposable upon that of the corresponding copper-free ferrocenium cation (**9**). This is not incompatible with the suggestion that (**8**) incorporates the ferrocenium cation, since the absorbance of the free ligand (**7**) is about a tenth of that of the cation (**9**). We suppose therefore that in the 2:1 complex (**8**) one of the two ferrocene nuclei was oxidized to a ferrocenium cation and the copper atom co-ordinated to the sulphur atoms in the thiamacrocycle moiety was reduced to Cu^{I}. This is also confirmed by the magnetic moments, the e.s.r. spectra, and the Mössbauer spectrum (see below).

Magnetic Properties.—The magnetic susceptibilities of powdered samples of the copper complexes (**2**), (**5**), and (**8**) and the copper-free ferrocenium cations, as tetrafluoroborate salts, (**3**), (**6**), and (**9**) were measured in the temperature range 80—300

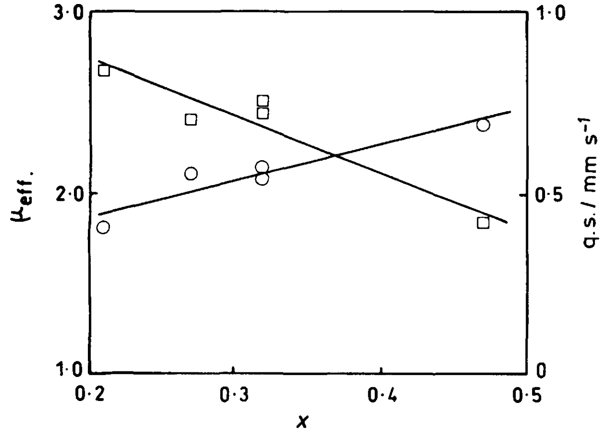


Figure 1. Correlation of the magnetic moments (○) and the quadrupole splitting (□) with the parameter of the low-symmetry contribution x

Table 3. Mössbauer parameters of the complexes and cations

Compound	T*/K	Q.s./mm s^{-1}	I.s./mm s^{-1}
(**2**)	r.t	0.28	0.42
	78 K	0.35	0.51
(**5**)	r.t.	0.42	0.42
	78 K	0.39	0.54
(**8**)	r.t.	2.38	0.45
		0.70	0.46
(**3**)	r.t.	0.75	0.45
(**6**)	r.t.	0.84	0.43
(**9**)	r.t.	0.72	0.44
(**4**)	r.t.	2.39	0.42
(**7**)	r.t.	2.36	0.43

* r.t. = Room temperature.

K using the Faraday method. Effective magnetic moments at 300 K are given in Table 2. The ground-state electronic configuration for ferrocenium cation has been established to be $^2E_{2g}(a_{1g})^2(e_{2g})^3$ by a combination of theoretical[24] and experimental results.[25—29] This state is orbitally degenerate and hence its magnetic moment deviates significantly from the spin-only value of 1.73. However, the magnetic moments of the sulphur-substituted ferrocenium cations (**3**), (**6**), and (**9**) (1.81—2.13) are only slightly smaller than those of the ferrocenium and alkylferrocenium cations (2.3—2.6).[30] This rather small deviation may be interpreted by taking into account the lowering of the axial symmetry, D_5, due to the sulphur substitution of a ferrocene nucleus. Complex (**8**) showed a magnetic moment similar to that of the ferrocenium cation (**9**), while the magnetic moments of the copper-containing complexes (**2**) and (**5**) were rather larger (*ca.* 0.5) than those of the ferrocenium cations (**3**) and (**6**), respectively, even though they did not deviate from those of ferrocenium cations. These results confirm that the copper-containing complexes involve the ferrocenium counterpart.

A plot of the effective magnetic moment *vs.* temperature for complexes (**2**) and (**5**) is very similar to that for the ferrocenium cations,[30] indicating no intramolecular exchange interaction.[31] The larger magnetic moments of complexes (**2**) and (**5**) compared with those of the cations (**3**) and (**6**) are likely due to the decrease in distortion from D_5 symmetry owing to the different fitting of the copper atom to the thiamacrocycle moiety rather than an interaction between the iron atom of a ferrocene moiety and the copper atom co-ordinated to sulphur atoms of the thiamacrocycle moiety, because such an increase in magnetic moment was not obtained in complex (**8**).

E.S.R. Spectra.—Electron-spin resonance signals were recorded at 78 K for the powdered sample. The copper-containing complexes (**2**), (**5**), and (**8**), as well as the ferrocenium cations (**3**), (**6**), and (**9**), showed a polycrystalline line shape that could be fitted with an axial g tensor. The observed $g_{\parallel}$ and $g_{\perp}$ values are summarized in Table 2. Ferrocenium and biferrocenium systems have been reported to have $g_{\parallel}$ in the range of 3.2—4.35 and $g_{\perp}$ in the range 1.91—1.26.[29,32] As shown in Table 2, for the sulphur-substituted ferrocenium cation, the $g_{\perp}$ values are near the upper limit of the range described above, but the $g_{\parallel}$ values deviate significantly from this range. The e.s.r. spectrum of the ferrocenium cation itself cannot be observed above 78 K because of the short relaxation time.[29] The success in detecting e.s.r. signals in the present case should be attributed to the lowered symmetry resulting in longer e.s.r. relaxation times as shown for the phenyl-substituted ferrocenium cations[29] and biferrocenium cations.[32] Prins[24] has given g value expressions appropriate for ferrocenium derivatives [equations (1) and (2)],

$$g_{\parallel} = g_z = 2 + 4kx/(1 + x^2)^{\frac{1}{2}} \qquad (1)$$

$$g_{\perp} = g_x = g_y = 2/(1 + x^2)^{\frac{1}{2}} \qquad (2)$$

where k and x are related to the degree of delocalization of the unpaired electron and to the magnitude of the low-symmetry perturbation, respectively. The parameters k and x were calculated for the present compounds from the $g_{\parallel}$ and $g_{\perp}$ values observed, and are summarized in Table 2. The values of k obtained here are comparable with those of other ferrocenium cations ($\approx$ 0.8),[24] while the values of x perturbation are significantly smaller than those of alkyl- and aryl-substituted ferrocenium ions (1.2—0.5).[24] This suggests that the low $g_{\parallel}$ value of the sulphur-substituted ferrocenium cations is mainly due to the low-symmetry distortion. However, the e.s.r.-delocalized species show $g_{\parallel}$ values in the range of 2.3—2.8 and $g_{\perp}$ close to 2.0.[33] We may not be able to ignore the small contribution of the delocalized unpaired electron through conjugation between a ferrocenyl ring and a sulphur lone pair to the lowering of the $g_{\parallel}$ values in the cations (**3**), (**6**), and (**9**). The e.s.r. parameters of the copper-containing complexes (**5**) and (**8**) are somewhat different from those of the corresponding sulphur-substituted ferrocenium cations (**6**) and (**9**), respectively, but are within the range of those of the ferrocenium cations, indicating that the former complexes contain a ferrocenium cation. The e.s.r. spectrum of (**2**) puzzlingly consisted of very broad features, and the g values could not be determined. This is probably due to the decrease in e.s.r. relaxation times, which stems from the close fitting of the copper atom to the hole of the thiamacrocycle, accompanied by the increased symmetry. For cations (**3**), (**6**), and (**9**), as well as the copper(I)-containing complexes (**2**), (**5**), and (**8**), the magnetic moments were plotted against the parameter x obtained from the e.s.r. measurements (Figure 1). A good linear relationship was obtained. This supports the conclusion that the effective magnetic moments also principally reflect the distortion of axial symmetry. The x value for complex (**2**), which gave only a broad e.s.r. signal, can be calculated to be 0.57 from the $\mu_{\text{eff.}}$ value by using the above relationship.

Mössbauer Spectra.—The Mössbauer spectra of the ferrocenium cations (**3**), (**6**), and (**9**) were measured at room temperature. The isomer shift (i.s.) and quadrupole splitting (q.s.) data are summarized in Table 3. A representative spectrum is shown in Figure 2 for the cation (**3**). The Mössbauer spectra of the copper-containing complexes (**2**) and (**5**) were measured at 78 K and room temperature and the parameters are summarized in Table 3. Their q.s. values are more similar to those of the corresponding ferrocenium cations than to that of the free ligand (**4**). The values observed for the copper-containing

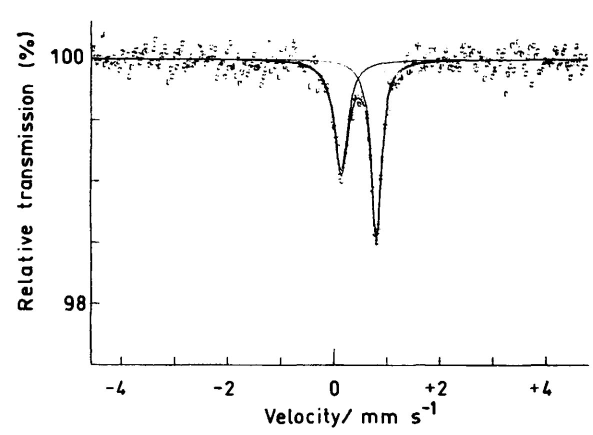
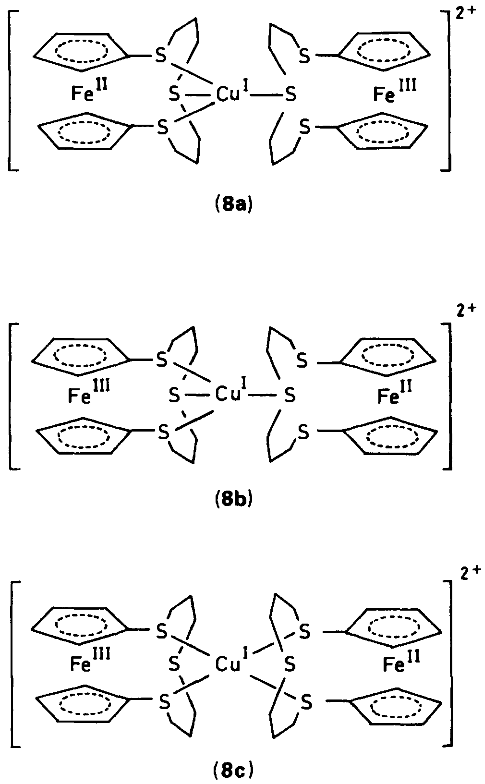


Figure 2. Mössbauer spectrum of the cation (**3**)



(**8a**)

(**8b**)

(**8c**)

Scheme 3.

complexes [0.39, (**5**) and 0.35 mm s^{-1}, (**2**)] are much smaller than those of the delocalized class III mixed-valence systems (1.78 mm s^{-1} for [0.0]ferrocenophane[14] and 1.667 mm s^{-1} for [2.2]ferrocenophane cations).[13,34] These facts indicate that the ferrocene moiety in the complexes (**2**) and (**5**) is oxidized to the ferrocenium cation, and that the positive charge is localized on the iron atom and not delocalized between the iron atom in a ferrocene nucleus and the copper atom incorporated in the thiamacrocycle. This is in agreement with the results obtained from other physicochemical measurements (see above).

It is well known[35,36] that ferrocene exhibits a doublet with a relatively large q.s. value (*ca.* 2.4 mm s^{-1}), while the q.s. value of the ferrocenium cation is nearly zero (0.0—0.08 mm s^{-1}). Interestingly, the sulphur-substituted ferrocenium cations (**3**), (**6**), and (**9**) showed relatively large q.s. values (*ca.* 0.7 mm s^{-1}). To our knowledge, such large values have not been reported for the simply substituted ferrocenium cations, except for that of diferrocenyl selenide (q.s. = 0.495 mm s^{-1}).[37] A substituent which can induce low-symmetry distortion or conjugate with a ferrocenyl nucleus tends to increase the q.s. value of the ferrocenium cation. The q.s. values of the sulphur-substituted ferrocenium cations and their copper(I)-containing complexes prepared in the present study cover a wide range. So, the q.s. values were plotted against the x values calculated from the e.s.r. parameters of the corresponding compounds (Figure 1). A good linear correlation was obtained. This strongly suggests that the large q.s. value of the sulphur-substituted ferrocenium cations is mainly due to the axial symmetry distortion, since the x value reflects the symmetry perturbation. Using this relationship, the q.s. value of complex (**2**) was calculated to be 0.30 mm s^{-1} from the x value obtained from the $\mu_{eff.}$ value mentioned in the previous section. This value is in excellent agreement with the measured value of 0.28 mm s^{-1}. These facts also support the suggestion described above. However, a slight extension of the conjugation of the sulphur lone pair may result in the increased q.s. values for the sulphur-substituted ferrocenium cations, since the q.s. values of the conjugated ferrocenium cations, for example, biferrocenium cations (q.s. = 0.288—0.400 mm s^{-1})[33,38] and the tri-iodide salt of diferrocenylacetylene (q.s. = 0.49 mm s^{-1}),[34] are also moderately large.

The Mössbauer spectrum of the 2:1 complex (**8**) had two quadrupole-split doublets, the outer of which had a q.s. value of 2.38 mm s^{-1} centred at 0.45 mm s^{-1} and the inner of which had a splitting value of 0.70 mm s^{-1} centred at 0.46 mm s^{-1}. The former Mössbauer parameter is similar to that of the free ligand (**7**) (q.s. = 2.36 mm s^{-1}) and the latter value is nearly consistent with that of the corresponding cation (**9**) (q.s. = 0.72 mm s^{-1}). This confirms that one of the two ferrocene nuclei in (**8**) is oxidized to the ferrocenium cation. Since the total charge of the complex is +2, the copper atom co-ordinated to the sulphur atoms seems to exist as Cu^{I}. It is interesting that the q.s. value of (**8**) resembles that of the ferrocenium cations (**3**) and (**6**), but not that of the copper-containing complexes (**2**) and (**5**). If complex (**8**) has the structure (**8b**) or (**8c**) (proposed in the preliminary report[39]) the q.s. value ought to be near that of (**2**) and (**5**) because of the similar structural requirement. The similarity to that of the cations (**3**) and (**6**) suggests an alternative structure (**8a**), in which the copper atom is not co-ordinated to the sulphur atoms bound to the oxidized ferrocene nucleus. This suggestion seems to be supported by the preliminary *X*-ray analysis data for (**8**).[40]

In conclusion, the results of various physicochemical measurements indicate that the copper-containing heterobimetallic complexes (**2**), (**5**), and (**8**) are class I type hetero mixed-valence compounds with charge-localized, non-interacting ferrocenyl and copper(I) groups. The question whether an intramolecular redox reaction producing such species takes place before or after the complex formation remains unexplained. Cyclovoltammetric measurement of the complex[11] of (**7**) with copper(I) perchlorate in acetonitrile showed only an irreversible wave for the redox reaction of the copper atom, suggesting that the copper(II) complex of (**4**) is unstable. It seems reasonable to assume that the redox reaction may occur at the stage of a partial co-ordination of copper(II) to a part of the thiamacrocycle (probably the two sulphur atoms connected directly to the ferrocene nucleus). In the present complexes (**2**), (**5**), and (**8**) the irreversible one-electron transfer from the iron atom in the ferrocene nucleus to the copper atom takes place probably in an intramolecular manner, while the reversible electron transfer changes [0.0]ferrocenophane[14] and [2.2]ferrocenophane-1,13-diyne[21,34] to the corresponding class III mixed-valence compounds, respectively. The irreversibility of the present complexes seems to stem from the fact that the intermediate complex in which the copper(II) atom is co-ordinated to the sulphur atoms of the thiamacrocycle is unstable because of the large difference in redox potential between Fe^{II}–Fe^{III} in ferrocene (−0.56 V *vs.* n.h.e., 90% EtOH)[41] and Cu^{I}–Cu^{II} in the copper complexes of macrocyclic tetrathioethers (0.67—0.80 V *vs.* n.h.e., 90% MeOH).[22,42]

Experimental

1,5,9,13-Tetrathia[13]- (**1**), 1,5,8,12-tetrathia[12]- (**4**), and 1,5,9-trithia[9]-(1,1′)ferrocenophanes (**7**) were prepared according to the method described in the literature.[8,11] Copper(II) tetrafluoroborate hydrate was commercially available.

The electronic spectra were recorded on a SHIMAZU UV-2100 spectrometer, i.r. spectra on a Hitachi 270-50 spectrometer. The magnetic moments were measured by using a Shimazu M2 magnetic balance. The e.s.r. spectra were recorded on a JEOL JES-PE-3X spectrometer.

(1,5,8,12-*Tetrathia*[12](1,1′)*ferrocenophanium*-S,S′,S″,S‴) *copper*(I) *Bis*(*tetrafluoroborate*) (**5**).—Solvent was saturated with nitrogen. To a solution of 1,5,8,12-tetrathia[12](1,1′)ferrocenophane (**4**) (85 mg, 0.2 mmol) in nitromethane (5 cm^3) was added a solution of copper(II) tetrafluoroborate hydrate (105 mg, 0.2 mmol) and acetic anhydride (0.2 cm^3, 0.8 mmol) in nitromethane (5 cm^3). After stirring for 15 min under nitrogen, diethyl ether (15 cm^3) was added. The solution was kept overnight in a refrigerator. The resulting black needles (90 mg, 68%) were collected by filtration. M.p. 203 °C (decomp.) (Found: C, 33.05; H, 3.75. $C_{18}H_{24}B_2CuF_8FeS_4$ requires C, 32.70; H, 3.65%).

(1,5,9,13-*Tetrathia*[13](1,1′)*ferrocenophanium*-S,S′,S″,S‴) *copper*(I) *Bis*(*tetrafluoroborate*) (**2**).—This was prepared by a method similar to that for (**5**). Black needles (92 mg, 68%). M.p. 218 °C (decomp.) (Found: C, 33.95; H, 3.95. $C_{19}H_{26}B_2CuF_8FeS_4$ requires C, 33.80; H, 3.90%).

(1,5,9-*Trithia*[9](1,1′)*ferrocenophane*-S,S′,S″)(1,5,9-*trithia* [9](1,1′)*ferrocenophanium*-S)*copper*(I) *Bis*(*tetrafluoroborate*) (**8**).—To a solution of 1,5,9-trithia[9]ferrocenophane (**7**) (72 mg, 0.2 mmol) in ethanol (10 cm^3) was added a solution of copper(II) tetrafluoroborate hydrate (103 mg, 0.2 mmol) in ethanol (5 cm^3) under nitrogen. The solution immediately turned brown. It was kept in a refrigerator for 2 h. The resulting dark brown powder (82 mg, 85%) was collected by filtration. The crystals were dissolved in dry acetone (15 cm^3) on warming, and the solution was diluted with hexane (4 cm^3) and kept overnight in a refrigerator. Black plates (53 mg, 55%) were collected by filtration. M.p. 191—193 °C (Found: C, 40.00; H, 4.25. $C_{32}H_{20}B_2CuF_8Fe_2S_6$ requires C, 39.80; H, 4.15%).

1,5,9,13-*Tetrathia*[13](1,1′)*ferrocenophanium Tetrafluoroborate* (**3**).—To a solution of 1,5,9,13-tetrathia[13](1,1′)ferrocenophane (70 mg, 0.16 mmol) and benzoquinone (18 mg, 0.17 mmol) in dry benzene (6 cm^3) was added 48% boron trifluoride–diethyl ether (0.1 cm^3, 0.8 mmol) under stirring. Brown oily crystals were immediately precipitated. Benzene was removed by decantation and the precipitates were washed with dry benzene then dissolved in refluxing acetone (10 cm^3). The solution was filtered and kept overnight in a freezer. The resulting black needles (55 mg, 65%) were collected by filtration. M.p. 250 °C (decomp.) (Found: C, 43.60; H, 5.10. $C_{19}H_{26}BF_4FeS_4$ requires C, 43.45; H, 5.00%).

1,5,8,12-Tetrathia[12](1,1′)ferrocenophanium tetrafluoroborate (**6**) was prepared in a similar manner as black plates (70 mg, 85%), m.p. 160 °C (decomp.) (Found: C, 42.35; H, 4.85. $C_{18}H_{24}BF_4FeS_4$ requires C, 42.30; H, 4.75%).

1,5,9-*Trithia*[9](1,1′)*ferrocenophanium Tetrafluoroborate* (**9**).—Prepared similarly as above. Black needles (45%, recrystallized from chloroform ethyl acetate). M.p. 140 °C (decomp.) (Found: C, 42.70; H, 4.45. $C_{16}H_{20}BF_4FeS_3$ requires C, 42.60; H, 4.45%).

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