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Synthesis and characterisation of copper complexes with N-ferrocenoyl-N'-aryl(alkyl)thioureas

Yao Feng Yuan [a], Ji Tao Wang [a], M. Concepción Gimeno [b], Antonio Laguna [b],*, Peter G. Jones [c]

[a] *Department of Chemistry, Nankai University, Tianjin 300071, China*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*
[c] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany*

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Abstract

The treatment of $CuCl_2 \cdot 2H_2O$ with ferrocenoyl-substituted thioureas of the type Fc–C(O)–NH–C(S)–N′HR (Fc = ferrocenyl; R = C_6H_5; C_6H_4-*p*-OMe; C_6H_4-*p*-C(O)Me; C_6H_4-*o*-Me; C_6H_4-*o*-Cl; C_6H_4-*o*-NO_2; *i*-Pr) gives the corresponding copper(I) derivatives with the metallic centre in an unusual coordination mode. The complexes were characterised by spectroscopic methods and X-ray diffraction studies. The electrochemical behaviour of these compounds was also investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper complexes; Ferrocenyl derivatives; Thioureas; Crystal structures

1. Introduction

It is well known that ferrocene has high electron density, aromaticity, stability and redox reversibility. The incorporation of redox-active ferrocene molecules into transition metal fragments is now opening promising fields of research [1–4]. Recently our work on ferrocenyl-substituted acylthiourea derivatives revealed that, because of the redox reversibility of ferrocene, it can be used as a probe to investigate the substituent effects, electron transfer and the interaction between metal centres by electrochemical methods [5–8].

With the simultaneous presence of S, N and O electron donors, the versatility and interesting behaviour of acylthioureas as building blocks in polydentate ligands for metal ions have become a topic of interest in the last few years. It has been reported that substituted acylthiourea ligands might act as monodentate sulfur donors, bidentate oxygen and sulfur or oxygen and nitrogen donors. They could also coordinate through the keto- or enol-thione form, depending of the ligands themselves, and the metal ions and counter-anions used [9–25] (see Table 1).

The structures of acylthiourea ligands have a significant effect on their resultant coordination chemistry. As a result of intramolecular hydrogen bonding, the thiourea N′–H moiety and the amidic O-donor atom form a six-membered ring, with the consequence that the ligands coordinate to metal centres in a monodentate fashion through the sulfur donor atom. For example, Cernak et al. [12] have prepared the complexes $[CuCl(ptu)_2]$, [CuCl(etu)], $[CuCl(btu)_2]$ (ptu: R = phenyl, etu: R = ethyl, btu: R = benzyl in $CH_3CH{=}CHC(O)$–NH–C(S)–NHR), which display this coordination mode, by the reaction of $CuCl_2$ with the corresponding derivatives of 2-propenoyl-thiourea. Furthermore, the ligand, N-benzoyl-N'-*n*-butylthiourea (H_2L) easily forms mixtures of *cis*- and *trans*-$[PtCl_2(H_2L)_2]$ complexes, in which the ligands bind in a monodentate fashion to the Pt(II) ion [26].

In contrast, the N',N'-disubstituted acylthiourea ligands, which do not form an intramolecular hydrogen bond, tend to coordinate predominantly in a bidentate (S, O) fashion to the transition metal ions through the

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* Corresponding author. Tel.: + 34-976-761 185; fax: + 34-976-761 187.

E-mail address: alaguna@posta.unizar.es (A. Laguna).

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sulfur and acyl oxygen atoms, e.g. in neutral mononuclear complexes [ML'_2], where M = Ni(II), Cu(II), Mn(II) and Co(III) and the ligands are *N*-ferrocenoyl-*N*′,*N*′-diethylthiourea [9]. The only notable exceptions to this mode of coordination of *N*′*N*′-disubstituted acylthiourea ligands can be seen in the complexes of Ag(I), Hg(II) and Au(I), in which the ligand binds the metal ion through the S atom only [17].

The coordination chemistry of substituted acylthioureas has led to some interesting practical applications, including liquid–liquid extraction, pre-concentration and highly efficient chromatographic separation, fluorimetric detection of the platinum group metals, and the selective on-line pre-concentration of ultra-traces of Pd, followed by its determination using graphite furnace atom absorption spectrometry [24,26]. The preliminary results have shown that the acylthiourea ligand could play an important role in the biological activity of mixed-ligand Pt(II) complexes and these Pt(II) complexes can thus be used as potential chemotherapeutic agents [27].

As part of our studies on ferrocene-containing substituted acylthioureas and their transition metal complexes [8], we report here on the synthesis and characterisation of the complexes formed by the reaction of $CuCl_2$ with ferrocenoyl-thiourea ligands, Fc–C(O)NH–C(S)NR^1R^2. The crystal structure of one of the complexes in this work shows the *N*-ferrocenoyl-*N*′-aryl(alkyl)thiourea ligand to display an unusual coordination mode to Cu(I). The crystal structures of two of the ligands are also described.

2. Results and discussion

2.1. Synthesis

We have studied the coordination behaviour of the ferrocenoyl-substituted thioureas Fc–C(O)–NH–C(S)–N′HR (R = C_6H_5 (**1**); C_6H_4-*p*-OMe, (**2**); C_6H_4-*p*-C(O)Me (**3**); C_6H_4-*o*-Me (**4**); C_6H_4-*o*-Cl (**5**); C_6H_4-*o*-NO_2 (**6**); *i*-Pr (**7**)) with $CuCl_2·2H_2O$. These ligands have been previously described by us and some preliminary studies provided evidence for intramolecular hydrogen bonds [28,30]. To confirm this, we have determined the crystal structure of two of the ligands used here, because the ligand structure is an important factor in determining in the coordination mode to the metal complexes. In both cases intramolecular hydrogen bonds between the NH and the carbonyl oxygen atom were observed. The reaction of the ligands with $CuCl_2·2H_2O$ at room temperature with alcohol as

Table 1
Some structural features for transition metal complexes of substituted acylthiourea ligands: R^1–C(O)–NH–C(S)–N′R^2R^3

No.	R^1	R^2	R^3	Central ion	Coordination atom	Coordination geometry	Reference
1	Fc [a]	Et [b]	Et	Ni(II)	O, S	*cis*-square planar	[9]
2	Fc	Py [c]	H	Fe(II)	O, N′, N″	octahedral	[10]
3	Fc	Me [d]	Me	Cu(II)	S bridge, Cl	dimer, distorted tetrahedral	[11]
4	Fc	Ar [e]	H	Cu(I)	S, Cl	planar triangle	this work
5	PE [f]	Ph [g]	H	Cu(I)	S, Cl; Cl or S bridge	dimer, distorted trigonal pyramidal	[12]
6	Ph	Et	Et	Cu(II)	O, S	tetrahedral	[13]
7	Ph	Et	Et	Ni(II), Pd(II)	O, S	*cis*-square planar	[14,15]
8	Ph	butyl	butyl	Pt(II)	O, S	*cis*-square planar	[16]
9	o-Cl–Ph	Et	Et	Ni(II)	O, S	*cis*-square planar	[17]
10	Ph	propyl	H	Pt(II)	S, (Cl)	*cis*-square planar	[18]
11	Na–Ph [h]	butyl	butyl	Pt(II)	O, S	*trans*-square planar	[19]
12	Ph	Et	Et	Ag(I)	O, (HS)	tetrahedral	[20]
13	Ph	Et	Et	Ru(III), Rh(III)	O, S	octahedral	[21,22]
14	Ph	alkyl	alkyl	Au(I)	S	linear	[23]
15	Ph	Ph	H	Rh(I)	O, S, N′-tridentate	dinuclear Rh(I), square planar and square-based pyramid	[24]
16	Ph	Py [i]	H	Cu(II)	O, S, Cl	dimer	[25]

[a] Fc, ferrocenoyl.
[b] Et, ethyl.
[c] Py, pyridyl.
[d] Me, methyl.
[e] Ar, Aryl.
[f] PE, propenyl, CH_3–CH=CH–
[g] Ph, phenyl
[h] NaPh, naphthyl
[i] Py, various substituted pyridine.

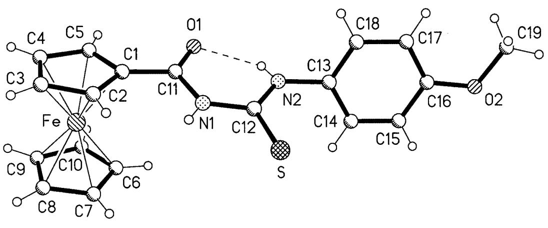

Fig. 1. Molecular structure of compound **2** in the crystal showing the atom numbering scheme.

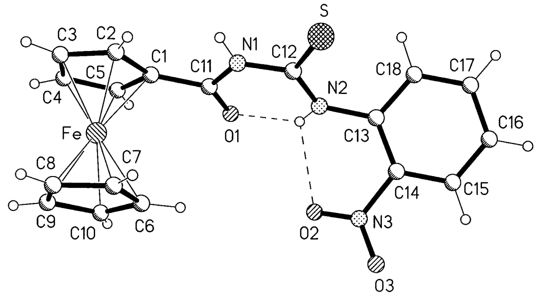

Fig. 2. The structure of one of the two independent molecules of compound **6** in the crystal with the atom labelling scheme.

solvent gives the new complexes [CuCl(FcCONHCSNHR)$_2$] (R = C_6H_5 (**8**); C_6H_4-*p*-OMe (**9**); C_6H_4-*p*-C(O)Me (**10**); C_6H_4-*o*-Me (**11**); C_6H_4-*o*-Cl (**12**); C_6H_4-*o*-NO_2 (**13**); *i*-Pr (**14**)). Elemental analysis, IR spectra, ^{1}H and ^{13}C NMR spectra and one crystal structure showed that they form Cu(I) complexes with an unusual coordination mode, very different from those reported in other related studies. These results are also different from those found by us in the reaction of ferrocenoyl-thioureas without intramolecular hydrogen bonds, of the type Fc–C(O)–NH–C(S)–NR^{1}R^2, in which N′R^{1}R^2=NEt$_2$, N(CH$_2$)$_5$, which with $CuCl_2$ at room temperature form mononuclear complexes very quickly. In the resulting Cu(II) complexes the ferrocenyl-thioureas act as bidentate ligands to Cu(II) via the acyl oxygen and sulfur atoms [8].

All the complexes are orange–red or red crystalline solids. They are soluble in DMF, DMSO, CH_2Cl_2 and $CHCl_3$, slightly soluble in EtOH, Me_2CO and Et_2O, but insoluble in non-polar solvents such as pentane and benzene. Their elemental analysis, IR spectra and ^{1}H and ^{13}C NMR spectra data are reported in Section 4.

2.2. Infrared spectra

The infrared spectra of the complexes show the following significant changes when compared with the spectra of the corresponding ligands. The most striking changes are observed for the C=S stretching frequency at approximately 1343 cm^{-1} in the free ligands, which disappears completely, or shifts to lower wavenumber and decreases in intensity. This is in agreement with the crystal structure determined for the copper complex **13** and suggests that the sulfur atom of the thiocarbonyl group is involved in coordination bonding. The stretching frequencies of N–H vibrations either decrease or form a weak and broad band along with that of N′–H at approximately 2900–3200 cm^{-1}. The C–N stretching vibration in CO–NH moiety shifts to higher wavenumber at 1277 cm^{-1}, as a moderately strong band. The intensity and wavenumber of ν(C=O) at 1663 cm^{-1} are essentially the same as in the free ligands. At the same time there appear two new absorption bands at 323 and 384 cm^{-1} in the far infrared region; the former is ascribed to ν(Cu–Cl) and the latter to ν(Cu–S) vibration.

2.3. NMR spectra

NMR spectra are very useful in determining whether the coordination reactions of ferrocenoyl-thioureas with Cu(II) chloride have take place. The ^{1}H and ^{13}C NMR spectra of the complexes are consistent with the structural results. The chemical shifts of N–H and N′–H increase by 1.30–2.00 and approximately 0.40 ppm, respectively, indicating an intermolecular hydrogen bonding between the N–H groups and the chloro atom coordinated to copper. The resonances for the cyclopentadienyl hydrogen atoms of the ferrocenyl group broaden appreciably; there is a downfield displacement of about 0.70 ppm for the α protons, whereas the β and the unsubstituted cyclopentadienyl ring protons are little changed. The fact that the resonances for the α protons of the cyclopentadienyl ring are shifted to lower field relative to those in the free ligands may be also be caused by the intramolecular hydrogen bonding between these protons and the chloro atom coordinated to copper (see X-ray comments below). From their ^{1}H NMR data, it can be inferred that the intramolecular hydrogen bonding is preserved on coordination and is present also in solution and not only in the solid state. The ^{13}C NMR spectra of these complexes do not show significant changes compared with those of the corresponding free ligands.

2.4. Crystal structure determinations

The previous investigations of the ferrocenoyl-thiourea ligands indicated intramolecular hydrogen bonds between carbonyl and N′–H groups in acyl-thiourea side chains [28,29]. We have established by X-ray diffraction studies the crystal structures of the ligands **2** and **6**; the molecules can be seen in Figs. 1 and 2, respectively. A selection of bond lengths and angles is collected in Tables 2 and 3, respectively.

In the structure of the ferrocenoyl-thiourea derivative Fc–C(O)–NH–C(S)–NH–C_6H_4-*p*-O–Me (**2**) the overall bond lengths and angles in the ferrocene and the thiourea moiety are normal, with a C(12)–S bond distance of 1.6740(17) Å and C(11)–O(1) distance of 1.222(5) Å, both typical of double bonds. The unit –N′H–C(S)–NH–C(O)– forms an intramolecular hydrogen bond N(2)–H(02)···O(1) (H···O 1.999(16) Å) to give a planar six-membered ring, which is almost parallel to the cyclopentadienyl ring of the ferrocene moiety. The same hydrogen atom acts as a weak intermolecular H bond donor to the methoxy oxygen atom, with H(02)···O(2) 2.507(18) Å, thus forming a highly asymmetric three-centre H bonding system. Finally, there is a non-classical H bond from a proton of the cyclopentadienyl ring, C(2)–H(2)···O(1) with H···O 2.55 Å.

The structure of Fc–C(O)–NH–C(S)–NH–C_6H_4-*o*-NO_2 (**6**) can be seen in Fig. 2, it crystallises with two independent molecules. In both molecules, the group N(2)–H(03) acts as donor for an intramolecular three-centre H bond to O(1) and O(2), with H···O(1) 1.972(18), 2.00(2) and H···O(2) 2.281(19), 2.31(2) Å. Weak intermolecular H bonds are formed from N(1)–H(02) to the thiourea sulfur, with H···S 2.84(2), 2.78(2) Å. There are also several intermolecular hydrogen bonds of the type C–H···O, of which the shortest are H(16)···O(1′) 2.38 Å and H(3)···O(2′) 2.45 Å.

Table 2
Selected bond lengths (Å) and angles (°) for compound **2**

Bond lengths			
S–C(12)	1.6740(17)	N(1)–C(12)	1.392(2)
O(1)–C(11)	1.225(2)	N(2)–C(12)	1.326(2)
O(2)–C(16)	1.3706(19)	N(2)–C(13)	1.430(2)
O(2)–C(19)	1.427(2)	C(1)–C(11)	1.474(2)
N(1)–C(11)	1.383(2)		
Bond angles			
O(1)–C(11)–N(1)	122.53(15)	N(1)–C(12)–S	118.16(13)
O(1)–C(11)–C(1)	122.42(15)	C(18)–C(13)–N(2)	119.16(15)
N(1)–C(11)–C(1)	115.04(15)	C(14)–C(13)–N(2)	120.81(15)
N(2)–C(12)–N(1)	116.71(15)	O(2)–C(16)–C(17)	123.97(15)
N(2)–C(12)–S	125.10(13)	O(2)–C(16)–C(15)	116.00(15)

Table 3
Selected bond lengths (Å) and angles (°) for compound **6**

Bond lengths			
S–C(12)	1.6661(15)	S′–C(12′)	1.6636(15)
O(1)–C(11)	1.2277(18)	O(1′)–C(11′)	1.2322(19)
N(1)–C(12)	1.3860(19)	N(1′)–C(11′)	1.3830(19)
N(1)–C(11)	1.3882(19)	N(1′)–C(12′)	1.3836(19)
N(2)–C(12)	1.341(2)	N(2′)–C(12′)	1.339(2)
N(2)–C(13)	1.4126(19)	N(2′)–C(13′)	1.4140(19)
C(1)–C(11)	1.468(2)	C(1′)–C(11′)	1.467(2)
Bond angles			
C(12)–N(1)–C(11)	129.20(14)	C(11′)–N(1′)–C(12′)	128.73(14)
C(12)–N(2)–C(13)	124.66(13)	C(12′)–N(2′)–C(13′)	124.89(13)
C(5)–C(1)–C(11)	124.52(14)	C(2′)–C(1′)–C(11′)	128.37(13)
C(2)–C(1)–C(11)	127.30(14)	C(5′)–C(1′)–C(11′)	123.14(14)
O(1)–C(11)–N(1)	122.77(14)	O(1′)–C(11′)–N(1′)	122.51(14)
O(1)–C(11)–C(1)	123.46(13)	O(1′)–C(11′)–C(1′)	122.64(13)
N(1)–C(11)–C(1)	113.77(13)	N(1′)–C(11′)–C(1′)	114.82(13)
N(2)–C(12)–N(1)	114.74(13)	N(2′)–C(12′)–N(1′)	115.26(13)
N(2)–C(12)–S	126.50(12)	N(2′)–C(12′)–S′	126.10(12)
N(1)–C(12)–S	118.71(12)	N(1′)–C(12′)–S′	118.59(12)
C(14)–C(13)–N(2)	122.36(15)	C(14′)–C(13′)–N(2′)	122.82(15)
C(18)–C(13)–N(2)	119.53(16)	C(18′)–C(13′)–N(2′)	119.45(15)

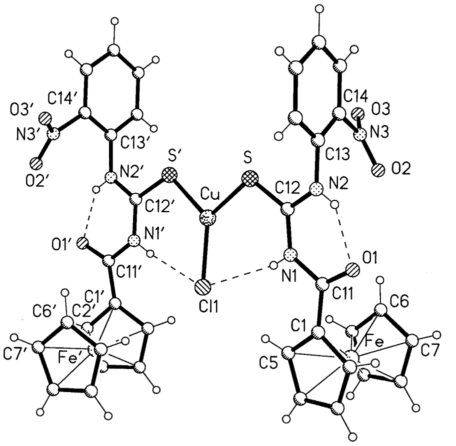

Fig. 3. The structure of complex **13** in the crystal showing the atom numbering scheme.

The structure of complex **13** has been established by X-ray diffraction and the molecule is shown in Fig. 3. A selection of bond lengths and angles is collected in Table 4. The Cu(I) atom is three-coordinated by the sulfur atoms of two different ligands and by one chlorine atom. This result is different from that found for the disubstituted ferrocenoyl-thioureas, where a four-coordinated copper derivative was found [9], and also for the Cu(I) complex with phenylthiourea, in which

Table 4
Selected bond lengths (Å) and angles (°) for complex **13**

Bond lengths			
Cu–Cl(1)	2.1876(6)	C(1)–C(11)	1.464(3)
Cu–S	2.2007(7)	S′–C(12′)	1.702(2)
Cu–S′	2.2057(6)	O(1′)–C(11′)	1.224(3)
S–C(12)	1.699(2)	N(1′)–C(12′)	1.372(3)
O(1)–C(11)	1.219(3)	N(1′)–C(11′)	1.401(3)
N(1)–C(12)	1.372(3)	N(2′)–C(12′)	1.326(3)
N(1)–C(11)	1.408(3)	N(2′)–C(13′)	1.421(3)
N(2)–C(12)	1.319(3)	C(1′)–C(11′)	1.465(3)
N(2)–C(13)	1.428(3)		
Bond angles			
Cl(1)–Cu–S	128.63(3)	N(1)–C(12)–S	122.19(18)
Cl(1)–Cu–S′	122.98(3)	C(18)–C(13)–N(2)	119.6(2)
S–Cu–S′	108.37(2)	C(12′)–S′–Cu	114.23(8)
C(12)–S–Cu	113.52(8)	C(12′)–N(1′)–C(11′)	125.8(2)
C(12)–N(1)–C(11)	126.0(2)	C(2′)–C(1′)–C(11′)	122.8(2)
C(5)–C(1)–C(11)	130.5(2)	C(5′)–C(1′)–C(11′)	129.4(2)
C(2)–C(1)–C(11)	121.5(2)	O(1′)–C(11′)–N(1′)	121.1(2)
O(1)–C(11)–N(1)	121.1(2)	O(1′)–C(11′)–C(1′)	121.7(2)
O(1)–C(11)–C(1)	122.6(2)	N(1′)–C(11′)–C(1′)	117.2(2)
N(1)–C(11)–C(1)	116.3(2)	N(2′)–C(12′)–N(1′)	117.9(2)
N(2)–C(12)–N(1)	117.8(2)	N(2′)–C(12′)–S′	119.06(17)
N(2)–C(12)–S	119.98(17)	N(1′)–C(12′)–S′	123.06(17)

there are two centrosymmetric dimeric molecules with tetracoordinated Cu(I) atoms [12]. The Cu–S bond distances are 2.2007(7) and 2.2057(6) Å, and as expected are shorter than those found in the above-mentioned tetra-coordinate complexes. The C–S distances, 1.699(2) and 1.702(2) Å, are longer than in the free ligand. The Cu–Cl bond length is 2.1876(6), again shorter than in the other copper-thiourea derivatives. The angles around the copper atom are slightly distorted from an ideal trigonal planar geometry, noticeably the narrow S–Cu–S angle of 108.37(2)°. This may be associated with the presence of intramolecular hydrogen bonds between the N(1)–H(01) and N(1′)–H(01′) groups and the chlorine atom of 2.92(2) and 2.67(2) Å, respectively (normalised to N–H 1.009 Å: 2.63 and 2.48 Å [31]) with angles of acceptable linearity 167(2) and 169(2)°. The cyclopentadiene hydrogens H5 and H5′ also make short contacts of 2.70 and 2.86 Å to the chlorine atom, which could be regarded as non-classical H bonds. There are further intramolecular hydrogen bonding systems involving the –N′H–C(S)–NH–C(O)– unit, forming two six-membered rings with distances for N(2)–H(02)···O(1) and N(2′)–H(02′)···O(1′) of 1.95(3) and 1.94(3) Å, respectively.

2.5. Cyclic voltammetric data

The cyclic voltammetric behaviour of the ligands and their copper complexes has been studied using CH_2Cl_2 as solvent. Attention was essentially centred on the ferrocene/ferrocenium redox couple in the ligands and their complexes. The anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, the formal reduction potential $E^{o\prime} = 0.5(E_{pa} + E_{pc})$, the separation ($\Delta E_p$) between the anodic and cathodic peak potentials and the ratio i_{pc}/i_{pa} of the experimentally determined anodic and cathodic peak current are given in Table 5. For comparison, the result of parent compound ferrocene is listed in the same table.

It can be seen from Table 5 that all the compounds exhibit one pair of redox peaks, corresponding to the Fe(II)/Fe(III) system. The electrochemical parameters indicate the chemical reversibility of the redox process, e.g. the i_{pc}/i_{pa} ratio is close to unity and the peak potential separation ΔE_p is in the range 50–90 mV.

The $E^{o\prime}$ values of the redox peaks in the ligands and their complexes are anodically shifted with respect to that of ferrocene (0.43 V), indicating that the acylthiourea groups exert predominately electron-withdrawing inducing effects, rendering oxidation more difficult.

All the complexes exhibit one reversible wave, which demonstrates that the two ferrocenyl fragments within ferrocenoyl-thiourea–copper complexes are electrochemically equivalent, simultaneously oxidised with no mutual interaction. However, no peaks corresponding to the oxidation process of the Cu(I)/Cu(II) couple are observed for the complexes in the scan potential range from 0 to 1.0 V and with scan rate 100 mV s^{-1}.

It seems that the nature of the substituent groups R in the Fc–C(O)–NH–C(S)–N′HR has a weak influence on the electrochemical properties of these ligands, i.e. 0.79 V (R = o-ClC_6H_4, C_6H_5), 0.78 V (o-$CH_3C_6H_4$, p-$OCH_3C_6H_4$) and 0.77 V (o-$NO_2C_6H_4$, i-Pr). However, we note that the substituent groups R have more influence on the redox behaviour of the ferrocenyl groups in these complexes, 0.75 V (R = o-$NO_2C_6H_4$), > 0.74 V (o-ClC_6H_4), > 0.72 V (C_6H_5, p-$OCH_3C_6H_4$, o-$CH_3C_6H_4$), > 0.69 V (i-Pr), which seems to show that the electronic effects of the substituents R on N′ can be delivered to the redox centre through the system

Table 5
Electrochemical data for the ligands and their copper complexes (V vs. SCE)

Compound	mV s^{-1}	E_{pa} (V)	E_{pc} (V)	$E^{o\prime}$(V) [a]	ΔE_p (mV) [b]	i_{pc}/i_{pa}
Ferrocene	100	0.47	0.39	0.43	80	1.06
1 $FcCONHCSNHC_6H_5$	100	0.82	0.75	0.79	70	1.03
2 $FcCONHCSNHC_6H_4$-p-OMe	100	0.81	0.74	0.78	70	1.04
4 $FcCONHCSNHC_6H_4$-o-Me	100	0.82	0.74	0.78	80	1.02
5 $FcCONHCSNHC_6H_4$-o-Cl	100	0.83	0.74	0.79	90	1.04
6 $FcCONHCSNHC_6H_4$-o-NO_2	100	0.81	0.73	0.77	80	1.07
7 FcCONHCSNH-i-Pr	100	0.81	0.73	0.77	80	1.10
8 $[CuCl(FcCONHCSNHC_6H_5)_2]$	100	0.75	0.69	0.72	60	1.05
9 $[CuCl(FcCONHCSNHC_6H_4$-p-$OMe)_2]$	100	0.76	0.68	0.72	80	0.97
11 $[CuCl(FcCONHCSNHC_6H_4$-o-$Me)_2]$	100	0.75	0.69	0.72	60	1.01
12 $[CuCl(FcCONHCSNHC_6H_4$-o-$Cl)_2]$	100	0.78	0.70	0.74	80	1.04
13 $[CuCl(FcCONHCSNHC_6H_4$-o-$NO_2)_2]$	100	0.77	0.72	0.75	50	1.07
14 $[CuCl(FcCONHCSNH$-i-$Pr)_2]$	100	0.72	0.66	0.69	60	0.90

[a] The redox potential values $E^{o\prime}$is formal reduction potential for a reversible couple and is defined by $E^{o\prime} = 0.5(E_{pa} + E_{pc})$.

[b] The reversibility of the oxidation wave implies $\Delta E_p = E_{pa} - E_{pc} \approx 60$ mV at 25 °C and $i_{pc}/i_{pa} \approx 1$, slow electron transfer at the electrode surface, 'irreversibility', cause the peak separation (ΔE_p) to increase.

of the σ-bonds and the intramolecular hydrogen bonding plane. These potential values are significantly lower than that of the free ligands, thus suggesting that the two ferrocene fragments in the complexes are easier to oxidise.

3. Conclusion

N-Ferrocenoyl-*N*′-aryl(alkyl)thiourea ligands act as unidentate ligands through the sulfur atom, forming strong complexes with the metal centre Cu(I). The coordination chemistry of *N*-ferrocenoyl-*N*′-aryl(alkyl)thiourea ligands (H_2L) is dominated by a strong intramolecular hydrogen bond which locks the thiourea N′–H moiety and amidic O-donor atom into a six-membered ring, with the consequence that the ligand coordinates to the Cu(I) ion through the S atom only, yielding $[Cu(H_2L)_2Cl]$ complexes. The Cu(II) was reduced to Cu(I) during the coordination process with oxidation of the ligand. A plausible explanation is that the higher affinity of the sulfur atom to Cu(I) evidently plays a certain role. At the same time, intramolecular hydrogen bonds of the type NH···Cl type may be assumed to contribute to the stabilisation of the Cu(I) complexes.

4. Experimental

4.1. General

Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Nicolet FT-IR 170 SX spectrometer with KBr pellets. Far-IR measurements were made with a Nicolet FT-IR 170 SX spectrophotometer by using Nujol mulls in the 100–500 cm^{-1} region.

All ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were recorded on a VG Autospec, with the FAB technique, using nitrobenzyl alcohol as matrix. Elemental analyses were carried out on a Perkin–Elmer 240C analyser. Melting points were determined on a PHMK (from Germany) melting point apparatus and were uncorrected. Cyclic voltammetric experiments were performed on a BAS-100B electrochemical analyser (Purdue Research Park, West Lafayette, Indiana, USA) equipped with a three electrode assembly with 0.1 mol^{-1} n-Bu_4NPF_6 as supporting electrolyte and CH_2Cl_2 as solvent. The working electrode was a platinum disk of 1.5 mm in diameter embedded in a cobalt glass seal and was polished consecutively with polishing alumina and diamond suspensions between runs. The reference electrode was a KCl saturated and blanketed with N_2 before the first scan. Measurements were made at r.t. (29 ± 3 °C). The voltammograms were scanned over the potential range 0–1.0 V (positive potential direction in forward mode), and the scan rates employed were 100 mV s^{-1}.

4.2. Synthesis of the ligands

The *N*-ferrocenoyl-*N*′-aryl(alkyl) thioureas were prepared according to literature methods [6,30].

4.3. Synthesis of the complexes

4.3.1. $[CuCl(FcCONHCSNHC_6H_5)_2]$ (**8**)

To a solution of **1** (0.364 g, 1 mmol) in C_2H_5OH (50 ml) was added dropwise $CuCl_2\cdot 2H_2O$ (0.0852 g, 0.5 mmol) in C_2H_5OH (20 ml). The reaction mixture was stirred for 8 h at r.t. The resulting orange–red precipitate was washed successively with C_2H_5OH, diethyl ether and petroleum ether (30–60 °C) prior to drying in vacuo. Compound **8** was obtained as orange–red crystals. Yield: 82%. m.p.: 164–167 °C dec. Elemental analysis, Found: C, 51.78; H, 3.89; N, 6.59. Calc. for $C_{36}H_{32}ClCuFe_2N_4O_2S_2$: C, 52.25; H, 3.91; N, 6.77%. NMR data; ^{1}H NMR ($CDCl_3$): 4.35 (s, 5H, C_5H_5), 4.57 (s, 2H, H^3, H^4–C_5H_4), 5.44 (s, 2H, H^2, H^5–C_5H_4), 7.30, 7.37, 7.45 (m, 5H, –C_6H_4), 10.51 (s, 1H, –NH), 13.04 (s, 1H, –N′H). ^{13}C NMR: 178.02 [–C(S)–], 175.0 [–C(O)–], 136.70, 129.15, 127.83, 125.65 (–C_6H_5), 71.49 (C^1 of C_5H_4), 70.64 (C_5H_5), 70.57 ($C^{3,4}$ of C_5H_4), 72.99 ($C^{2,5}$ of C_5H_4). IR (KBr pellets, cm^{-1}): ν(N–H) and ν(N′–H) 2900–3230 (w, br), ferrocenyl group: 3090 (w), 1376 (w), 1105 (m), 1000 (m), 908 (w), 826 (m), 498 (m), ν(C=O) 1663 (s), δ(CNH) 1507 (vs), ν(C–N) [–N–C(S)–N] 1154 (m), ν(C–N) [–C(O)–NH] 1278 (m), ν(C=S) 1343 (w).

The synthesis of complexes **9**–**14** proceeds in a similar manner to compound **8**; thus only the spectroscopic data will be given.

4.3.2. $[CuCl(FcCONHCSNHC_6H_4\text{–}OMe)_2]$ (**9**)

Color: orange–red. Yield: 76%, 0.336 g. m.p.: 167–172 °C dec. Recystallisation from a $CHCl_3$–petroleum ether (90–120 °C) solution gave X-ray quality crystals. Elemental analysis, Found: C, 51.34; H, 4.15; N, 6.41. Calc. for $C_{38}H_{36}Fe_2ClCuN_4O_4S_2$: C, 51.42; H, 4.10; N, 6.31%. NMR data; ^{1}H NMR ($CDCl_3$): 4.36 (s, 5H, C_5H_5), 4.58 (s, 2H, H^3, H^4–C_5H_4), 5.44 (s, 2H, H^2, H^5–C_5H_4), 3.80 (s, 3H, –OMe), 6.88, 6.91 (d, 2H, –C_6H_4), 7.34, 7.37 (d, 2H, –C_6H_4), 10.52 (s, 1H, –NH), 12.84 (s, 1H, –N′H). ^{13}C NMR: 178.80 [–C(S)–], 174.83 [–C(O)–], 158.94, 129.64, 127.01, 114.28 (–C_6H_4), 71.70 (C^1 of C_5H_4), 70.59 (C_5H_5), 70.53 ($C^{3,4}$ of C_5H_4–), 72.89 ($C^{2,5}$ of C_5H_4), 55.41 (–OMe). IR (KBr pellets, cm^{-1}): ν(N–H) 3213.7 (w), ν(N–H) 2960–3082 (w, br), ferrocenyl group: 3082 (w), 1376 (w), 1105 (m), 1031 (m), 900 (w), 834 (m), 482 (m), ν(C=O) 1663 (s), δ(CNH)

1507 (vs), δ(CNH) 1507 (vs), ν(C–N) [–N–C(S)–N] 1146 (vs), ν(C–N) [–C(O)–NH] 1277 (m), ν(C=S) 1304 (w). MS(FAB+), m/z (%) = 852 (12) $[M-\mathrm{Cl}]^+$.

*4.3.3. [CuCl(FcCONHCSNHC$_6$H$_4$-p-C(O)CH$_3$)$_2$] (**10**)*

Color: orange–red. Yield: 79%. m.p.: 171–172 °C dec. Elemental analysis, Found: C, 52.93; H, 4.05; N, 5.94. Calc. for $C_{40}H_{36}ClCuFe_2N_4O_4S_2$: C, 52.70; H, 4.00; N, 6.15%. NMR data; ^{1}H NMR (CDCl$_3$): 4.36 (s, 5H, C_5H_5), 4.60 (m, 2H, H^3, H^4–C_5H_4), 5.43 (m, 2H, H^2, H^5–C_5H_4), 2.57 [s, 3H, –C(O)–Me], 7.66, 7.69 (d, 2H, –C_6H_4), 7.95, 7.98 (d, 2H, –C_6H_4), 10.54 (s, 1H, –NH), 13.30 (s, 1H, –N′H). ^{13}C NMR: 197.05 [–C(S)–], 178.39, 174.93 [–C(O)–], 140.92, 135.59, 129.34, 124.85 (–C_6H_4), 71.35 (C^1 of C_5H_4), 70.66 (C_5H_5), 70.44 (C^{3,4} of C_5H_4), 73.15 (C^{2,5} of C_5H_4), 26.52 (Me). IR (KBr pellets, cm^{-1}): ν(N–H) and ν(N′–H) 2900–3255 (w, br), ferrocenyl group: 3091 (w), 1376 (w), 1105 (m), 1009 (m), 909 (w), 843 (m), 498 (m), ν(C=O) 1680 (s), δ(CNH) 1507 (vs), ν(C–N) [–N–C(S)–N] 1155 (m), ν(C–N) [–C(O)–NH] 1269 (vs), ν(C=S) 1335 (w).

*4.3.4. [CuCl(FcCONHCSNHC$_6$H$_4$-o-Me)$_2$] (**11**)*

Color: orange–red. Yield: 76%. m.p.: 167–172 °C dec. Elemental analysis, Found: C, 53.11; H, 4.28; N, 6.95. Calc. for $C_{38}H_{36}ClCuFe_2N_4O_2S_2$: C, 53.34; H, 4.25; N, 6.55%. NMR data; ^{1}H NMR (CDCl$_3$): 4.41 (s, 5H, C_5H_5), 4.62 (m, 2H, H^3, H^4–C_5H_4), 5.43 (m, 2H, H^2, H^5–C_5H_4), 2.31 [s, 3H, –Me], 7.54 (s, 1H, –C_6H_4), 7.27 (s, 3H, –C_6H_4), 10.44 (s, 1H, –NH), 12.61 (s, 1H, –N′H). ^{13}C NMR: 179.40 [–C(S)–], 174.2 [–C(O)–], 135.93, 133.90, 130.87, 128.07, 126.92, 126.55 (–C_6H_5), 71.83 (C^1 of C_5H_4), 70.57 (C_5H_5), 70.22 (C^{3,4} of C_5H_4), 72.81 (C^{2,5} of C_5H_4), 17.84 (–CH$_3$). IR (KBr pellets, cm^{-1}): ν(N–H) and ν(N′–H) 3189–3074 (w, br), ferrocenyl group: 3073 (w), 1376 (w), 1105 (m), 1023 (m), 909 (w), 818 (m), 490 (m), ν(C=O) 1655 (s), δ(CNH) 1523 (vs), ν(C–N) [–N–C(S)–N] 1163 (m), ν(C–N) [–C(O)–NH] 1269 (m), ν(C=S) 1343 (w). MS(FAB+), m/z (%) = 820 (22) $[M-\mathrm{Cl}]^+$.

*4.3.5. [CuCl(FcCONHCSNHC$_6$H$_4$-o-Cl)$_2$] (**12**)*

Color: orange–red. Yield: 79%. m.p.: 180–181 °C dec. Elemental analysis, Found: C, 48.54; H, 3.31; N, 6.34. Calc. for $C_{36}H_{30}Fe_2N_4O_2S_2CuCl_3$: C, 48.23; H, 3.38; N, 6.25%. NMR data; ^{1}H NMR (CDCl$_3$): 4.35 (s, 5H, C_5H_5), 4.59 (m, 2H, H^3, H^4–C_5H_4), 5.43 (m, 2H, H^2, H^5–C_5H_4), 7.41–7.35 (m, 4H, –C_6H_4), 10.53 (s, 1H, –NH), 13.07 (s, 1H, –N′H). ^{13}C NMR: 178.64 [–C(S)–], 175.01 [–C(O)–], 135.20, 133.36, 129.31, 126.88 (–C_6H_5), 71.35 (C^1 of C_5H_4), 70.61 (C_5H_5), 70.55 (C^{3,4} of C_5H_4), 73.06 (C^{2,5} of C_5H_4). IR (KBr pellets, cm^{-1}): ν(N–H) and ν(N′–H) 3189–3000 (w, br), ferrocenyl group: 3074 (w), 1376 (w), 1113 (m), 1006 (m), 909 (w), 818 (m), 490 (m), ν(C=O) 1655 (s), δ(CNH) 1515 (vs), ν(C–N) [–N–C(S)–N] 1162 (m), ν(C–N) [–C(O)–NH] 1269 (m), ν(C=S) 1318 (w).

*4.3.6. [CuCl(FcCONHCSNHC$_6$H$_4$-o-NO$_2$)$_2$] (**13**)*

Color: orange–red. Yield: 81%. m.p.: 142–144 °C dec. Crystals suitable for X-ray diffraction studies were obtained from CHCl$_3$–petroleum ether solution (90–120 °C). Elemental analysis, Found: C, 46.89; H, 3.32; N, 9.23. Calc. for $C_{36}H_{30}ClCuFe_2N_6O_6S_2$: C, 47.12; H, 3.30; N, 9.16%. NMR data; ^{1}H NMR (CDCl$_3$): 4.34 (s, 5H, C_5H_5), 4.58 (m, 2H, H^3, H^4–C_5H_4), 5.22 (m, 2H, H^2, H^5–C_5H_4), 7.3–8.2 (m, 4H, –C_6H_4), 9.94 (s, 1H, –NH), 13.49 (s, 1H, –N′H). ^{13}C NMR: 179.57 [–C(S)–], 172.93 [–C(O)–], 142.97, 133.62, 132.01, 129.20, 127.49, 125.35 (–C_6H_5), 71.52 (C^1 of C_5H_4), 70.63 (C_5H_5), 69.82 (C^{3,4} of C_5H_4), 73.03 (C^{2,5} of C_5H_4). IR (KBr pellets, cm^{-1}): ν(N–H) and ν(N′–H) 2640–3189 (w, br), ferrocenyl group: 3082 (w), 1376 (w), 1105 (m), 1031 (m), 916 (w), 818 (m), 490 (m), ν(C=O) 1655 (s), δ(CNH) 1507 (vs), ν(C–N) [–N–C(S)–N] 1163 (m), ν(C–N) [–C(O)–NH] 1277 (m), ν(C=S) 1343 (w).

*4.3.7. [CuCl(FcCONHCSNH-i-C$_3$H$_7$)$_2$] (**14**)*

Color: orange–red. Yield: 64%. m.p.: 178–179 °C dec. Elemental analysis, Found: C, 47.34; H, 4.50; N, 7.07. Calc. for $C_{30}H_{36}ClCuFe_2N_4O_2S_2$: C, 47.44; H, 4.79; N, 7.38%. NMR data; ^{1}H NMR (CDCl$_3$): 4.30 (s, 5H, C_5H_5), 4.48 (m, 2H, H^3, H^4–C_5H_4), 5.27 (m, 2H, H^2, H^5–C_5H_4), 1.28 (s, 7H, i-C_3H_7), 10.02 (s, 1H, –NH), 11.04 (s, 1H, –N′H). ^{13}C NMR: 177.38 [–C(S)–], 173.96 [–C(O)–], 72.14 (C^1 of C_5H_4), 70.41 (C_5H_5), 69.97 (C^{3,4} of C_5H_4), 72.50 (C^{2,5} of C_5H_4), 47.55 (–CH–), 21.67 (–CH$_3$). IR (KBr pellets, cm^{-1}): ν(N–H) and ν(N′–H) 3262–3156 (w, br), ferrocenyl group: 3082 (w), 1376 (w), 1100 (m), 999 (m), 917 (w), 826 (m), 490 (m), ν(C=O) 1663 (s), δ(CNH) 1515 (vs), ν(C–N) [–N–C(S)–N] 1146 (m), ν(C–N) [–C(O)–NH] 1277 (m), ν(C=S) 1352 (w).

4.4. Crystallography

The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (**2**: Siemens P4, −100 °C; **6**, **13**: Bruker SMART 1000 CCD, −130 °C). Data were collected using monochromated Mo Kα diffractometer (λ = 0.71073). An absorption correction was applied for **2** on the basis of Ψ-scans, for **6** on the basis of multiple scans with the program SADABS and for **13** by numerical methods following face-indexing. The structures were solved by direct methods and refined on F^2 using the program SHELXL-97 [32]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the NH groups were refined freely, methyls as rigid groups and other H atoms using a riding model. The absolute structure of **2** was determined by the Flack parameter

Table 6
Details of data collection and structure refinement for the compounds **2**, **6** and **13**

Compound	**2**	**6**	**13**·$CHCl_3$
Chemical formula	$C_{19}H_{18}FeN_2O_2S$	$C_{18}H_{15}FeN_3O_3S$	$C_{37}H_{31}C_{l4}CuFeN_6O_6S_2$
Crystal habit	red prism	red plate	red plate
T (°C)	-100	-130	-130
λ (Å)	0.71073	0.71073	0.71073
Crystal system	tetragonal	monoclinic	triclinic
Space group	$P\bar{4}2_1c$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
a (Å)	19.0602(12)	21.9441(16)	11.0605(10)
b (Å)	19.0602(12)	6.9820(9)	11.8267(10)
c (Å)	9.7138(14)	22.0803(18)	15.7000(14)
α (°)	90	90	85.131(3)
β (°)	90	95.237(3)	79.420(3)
γ (°)	90	90	85.310(3)
U (Å^3)	3528.9(6)	3368.9(6)	2006.9(3)
Z	8	8	2
D_{calc} (g cm^{-3})	1.484	1.614	1.716
M	394.26	409.24	1036.84
$F(000)$	1632	1680	1048
Crystal size (mm)	0.60 × 0.40 × 0.30	0.42 × 0.33 × 0.07	0.20 × 0.15 × 0.03
$2\theta_{max.}$ (°)	55	56.5	56.5
μ(Mo Kα) (cm^{-1})	9.9	10.4	16.6
Transmission	0.734–0.830	0.677–0.928	0.730–0.953
Reflections measured	8448	36 598	27 956
Unique reflections	4049	8379	9928
R_{int}	0.020	0.040	0.048
R [a]($F>4\sigma(F)$)	0.0225	0.0293	0.0348
wR [b](F^2, all reflections)	0.0509	0.0776	0.0818
Parameters	236	485	552
Restraints	2	0	348
S [c]	1.00	1.01	0.95
Max. $\Delta\rho$ (e Å^{-3})	0.17	0.41	0.84

[a] $R(F)=\Sigma\,\|F_o|-|F_c\|/\Sigma\,|F_o|$.

[b] $wR(F^2)=[\Sigma\,\{w(F_o^2-F_c^2)^2\}/\Sigma\,\{w(F_o^2)^2\}]^{0.5}$; $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$, where $P=[F_o^2+2F_c^2]/3$ and a and b are constants adjusted by the program.

[c] $S=[\Sigma\,\{w(F_o^2-F_c^2)^2\}/(n-p)]^{0.5}$, where n is the number of data and p is the number of parameters.

$x=0.011(11)$. The chloroform of solvation of compound **13** is disordered over two positions. To improve stability of refinement, weak U value restraints were employed (SIMU). Further crystal data are given in Table 6.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 157407-9 for compounds **2**, **6** and **13**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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