

A double sandwich silver(I) polymer with 1,1'-bis(diethyldithiocarbamate)-ferrocene

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The polymeric complex $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]_n[\text{ClO}_4]_n$, in which the silver centres are bonded to two sulfur atoms of different ferrocene moieties and also to the cyclopentadienyl rings in an η^2 fashion, is reported.

In the last few years the chemistry of ferrocene and the design of new compounds containing the ferrocene unit has received much attention, associated with utility in many fields such as organic synthesis, catalysis and material chemistry.^{1,2} Numerous derivatives in which the metallocene is bonded to a chelate ligand have been described. Interesting effects such as redox-switched bonding of metal ions within ferrocene crown ethers or investigations into the potential use of such compounds as amperometric sensors for metal ions or protons have been among the highlights of this development.^{3–8} It seems that the performance of such molecular devices depends on the efficient electronic communication between the ferrocene and the metal ion coordinated within the chelating ligand.

The compound 1,1'-bis(diethyldithiocarbamate)ferrocene, $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ [$\text{Fc} = \text{Fe}(\text{C}_5\text{H}_4)_2$], although synthesized more than ten years ago,⁹ has not been studied as a ligand. Here we report on the reaction of $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ with AgClO_4 to give a polymeric chain with stoichiometry $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]_n[\text{ClO}_4]_n$, in which the silver centres are bonded to two sulfur atoms of different ferrocene moieties and are also bonded to the cyclopentadienyl rings in an η^2 fashion. Thus the silver atoms can be regarded as being four-coordinate and the molecule as a double sandwich of iron and silver. This is the first example where an η^5 -Cp ring of the ferrocene unit is bonded to another metal centre through the π system. Recently Grossel *et al.* suggested the presence of a stabilising interaction between the metallocene π system of ferrocenyl substituted aza crown ethers and the crown bound to the crown moiety.¹⁰ The complex $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]_n[\text{ClO}_4]_n$ will be interesting in order to study the physical properties, mainly due to the possible existence of the delocalized aromatic conduction electrons.

The reaction of $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ with AgClO_4 (1 : 1 molar ratio) in diethyl ether gives a yellow precipitate from which the

complex $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]_n[\text{ClO}_4]_n$ **1** (Scheme 1) can be isolated.[‡] It is stable to air and moisture and behaves as a 1 : 1 electrolyte in acetone. The ¹H NMR spectrum is in agreement with the presence of one type of 1,1'-bis(diethyldithiocarbamate)ferrocene ligand. The positive liquid secondary-ion mass spectrum shows the peak $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$ at $m/z = 589$ as the most intense.

The structure of complex **1** has been confirmed by an X-ray diffraction study (Fig. 1).[§] The molecule consists of 1,1'-bis(diethyldithiocarbamate)ferrocene units bridged by silver atoms. Each silver centre is coordinated to sulfur atoms of different ferrocene moieties. The silver atom lies on an inversion centre and the iron atom on a twofold axis; consequently only half of the monomeric formula unit represents the asymmetric unit. Of necessity the grouping $\text{S}-\text{Ag}-\text{S}^i$ ($i = -x + 1, -y + 1, -z + 1$) is perfectly linear; additionally, the silver centre is weakly bonded to two carbon atoms of each of two cyclopentadienyl rings. The $\text{Ag}-\text{C}$ distances, 2.972(8) and 3.027(8) Å, are only slightly longer than the longest found in complexes of silver(I) with aromatic systems (2.47–2.92 Å).^{11–20}

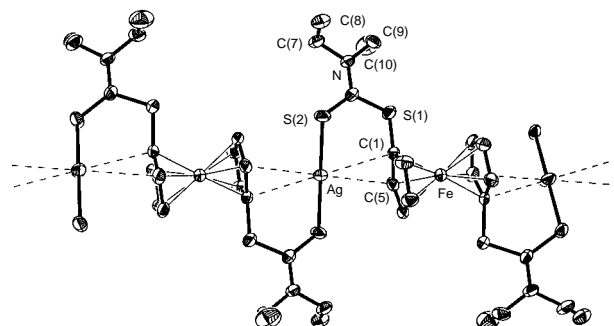
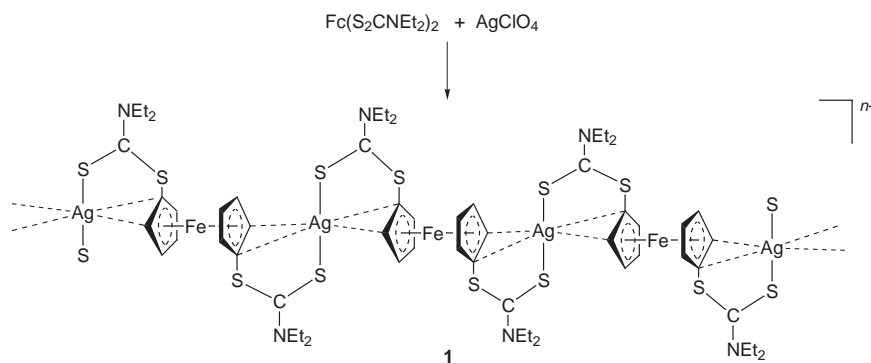


Fig. 1 Part of the polymeric chain of the cation of complex **1** in the crystal showing the atom numbering scheme. Ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.



Scheme 1

It is also noteworthy that aromatic silver(I) complexes usually show an asymmetry in their Ag–C interactions (as do copper complexes).^{21,22} According to Mulliken's model²³ the most favourable position for a silver ion is at the point of highest π -electron density, directly above one of the carbon atoms of the ring. Dewar²⁴ maintained that silver(I) could act not only as an electron acceptor, but also as a donor of electrons from a filled d orbital to an empty molecular orbital of the aromatic. If this 'back donation' interaction is of importance in the stabilization of the complex, the best overlap is achieved when the silver is located in the π cloud equidistant between the two carbon atoms. This situation has only been observed for naphthalene-tetrakis(silver perchlorate) tetrahydrate (2.59, 2.61 Å).¹⁹ In complex **1** the interaction is weaker, as discussed above.

The interaction of the silver atom with the C(1)–C(5) bond produces only a small effect on the ring geometry, as was previously observed in other silver–aromatic species. However the C(1)–C(5) bond is marginally longer at 1.448(11) Å, although the difference may not be significant, while the C₅ ring remains planar ($\sigma = 0.003$ Å).

The Ag–S(2) distance is 2.386(3) Å and compares well with those observed for linear Ag–S bonds in complexes such as [Ag₂(CH₂PPh₂S)₂] [2.382(3) Å].²⁵

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Notes and References

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‡ *Preparation*: to a solution of AgClO₄ (0.1 mmol, 0.021 g) in diethyl ether Fc(S₂NET₂)₂ (0.1 mmol, 0.048 g) was added. The mixture was stirred for 1 h and the resulting yellow solid filtered off and dried *in vacuo*. Yield 60%. Elemental analysis (%): Calc. for C₂₀H₂₈AgClFeN₂O₄S₄: C, 34.9; H, 4.1; N, 4.05; S, 18.65. Found: C, 34.95; H, 4.35; N, 4.25; S, 18.70%. ¹H NMR (300 MHz, CDCl₃), δ 4.46 (m, br, 4 H, C₅H₄), 4.38 (m, br, 4 H, C₅H₄), 3.94 (m, br, 4 H, CH₂CH₃), 3.77 (m, br, 4 H, CH₂CH₃), 1.33 (m, br, 6 H, CH₂CH₃), 1.18 (m, br, 6 H, CH₂CH₃).

§ *Crystal data*: [Ag{Fc(S₂CNET₂)₂}]_n[ClO₄]_m · 1.2CH₂Cl₂ · C₂₂H₃₂AgCl₅FeN₂O₄S₄, *M* = 857.71, monoclinic, space group *C2/c*, *a* = 20.066(5), *b* = 9.859(3), *c* = 18.463(5) Å, β = 113.02(2)°, *U* = 3362(2) Å³, *Z* = 4, μ (Mo-K α) = 1.69 mm⁻¹. A yellow plate 0.35 × 0.25 × 0.04 mm was used to collect 2935 reflections with intensities to $2\theta_{\max}$ 50°, of which 2924 (*R*_{int} = 0.018) were unique. The structure was solved by direct methods and

subjected to full-matrix least-squares refinement on *F*² (SHELXL-93). Refinement proceeded to *wR*(*F*²) = 0.17 for 2924 reflections, 183 parameters and 26 restraints, conventional *R*(*F*) [*I* > 2 σ (*I*)] 0.064. CCDC 182/891.

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