

## Synthesis of the First Diferrocenyl–Dithiolene Metal Complex: Bis(ferrocenylethylene-1,2-dithiolato) Nickelate(II)

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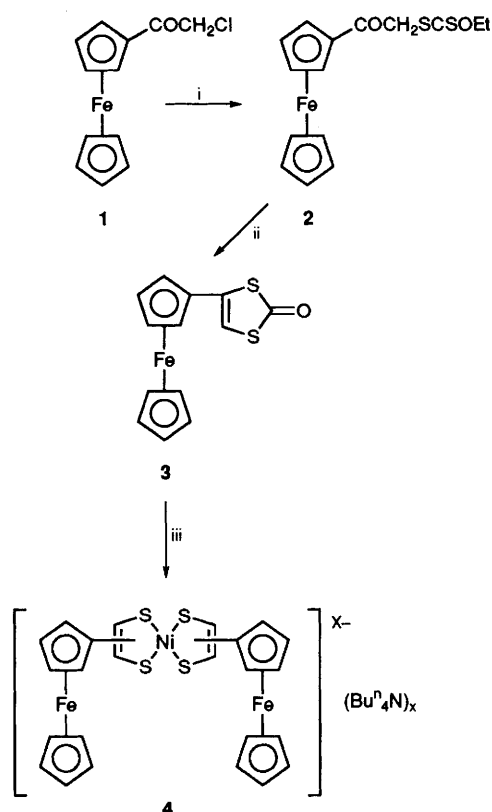
The synthesis and solution redox properties of the first diferrocenyl–dithiolene metal complex, bis(ferrocenylethylene-1,2-dithiolato) nickelate(II) are reported together with the X-ray crystal structure of the ligand precursor, 4-ferrocenyl-1,3-dithiole-2-one.

In recent years, both the chemistry of ferrocenes and dithiolene metal complexes, have gained renewed interest, especially within the growing areas of 'new materials science'.<sup>1–4</sup> Ferrocenes have potential for use in electrical devices since the iron(II)–iron(III) redox couple is highly dependent on the cyclopentadienyl substituents. This has opened up a new area of molecular conductors based on the incorporation of redox-active organometallics into the multi-sulfur  $\pi$ -acceptor ligands of transition metal bis(dithiolene) complexes.<sup>5</sup> The combination of metallocenes and dithiolenes in a single moiety would be expected to change the unusual electrical conduction, magnetic and optical properties already

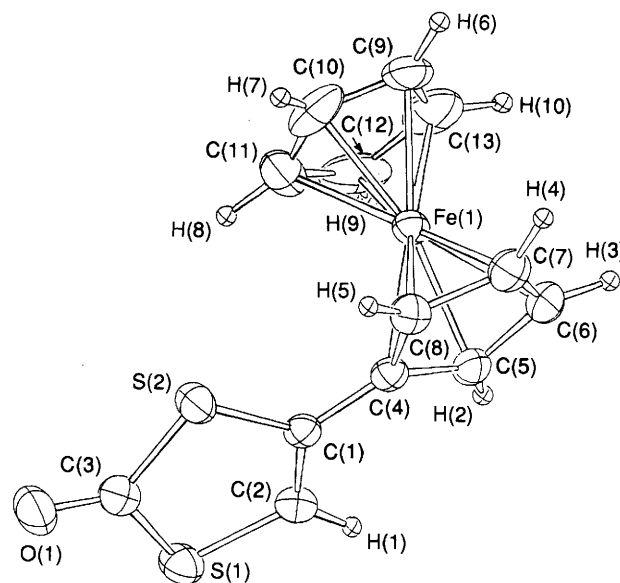
found for metal dithiolene complexes.<sup>6</sup> We now report the successful attachment of two ferrocene moieties to a nickel bis(dithiolene) core (complex 4), detailing the electrochemical properties together with the X-ray crystal structure of the ligand precursor 3.

Complex 4 was prepared as shown in Scheme 1.<sup>†</sup> Compound 2 was obtained as a dark-orange oil in 95% yield by the reaction of the  $\alpha$ -chloroketone 1 with potassium *o*-ethylxanthate in acetone. The addition of 2 (with stirring) to 98% sulfuric acid yielded 3,<sup>‡</sup> upon cooling in an ice-bath and subsequent work-up, as an orange powder (67%). Treatment of 3 with sodium ethoxide in ethanol at room temp., followed by addition of Bu<sup>n</sup><sub>4</sub>NBr and NiCl<sub>2</sub>·6H<sub>2</sub>O in ethanol yielded, after recrystallisation, complex 4<sup>§</sup> as a dark brown neutral complex, which is sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub>.

Crystals of 3 were obtained by slow evaporation of a chloroform solution and the structure was determined by single crystal X-ray diffraction.<sup>¶</sup> The most obvious feature of



**Scheme 1** Reagents and conditions: i, K<sub>2</sub>S<sub>2</sub>C(OEt)–acetone, 20 °C, 1 h; ii, 98% H<sub>2</sub>SO<sub>4</sub>, 0 °C, 1 h; iii, NaOEt–EtOH, 20 °C, 40 min then Bu<sup>n</sup><sub>4</sub>NBr, NiCl<sub>2</sub>·6H<sub>2</sub>O



**Fig. 1** X-Ray crystal structure of 3. Selected bond lengths (Å): Fe(1)–C(4) 2.041(4), Fe(1)–C(5) 2.040(4), Fe(1)–C(6) 2.037(5), Fe(1)–C(7) 2.044(5), Fe(1)–C(8) 2.029(5), C(1)–C(4) 1.456(6), C(3)–O(1) 1.197(6), C(1)–C(2) 1.326(6), C(1)–S(2) 1.739(4), S(1)–C(3) 1.735(5), S(2)–C(3) 1.744(5).

**Table 1** Half-wave redox potentials for ferrocene and compounds 3 and 4<sup>a</sup>

Redox process	[ML <sub>2</sub> ] <sup>2-</sup> ⇌ [ML <sub>2</sub> ] <sup>1-</sup> E <sup>‡</sup> ΔE	[ML <sub>2</sub> ] <sup>1-</sup> ⇌ [ML <sub>2</sub> ] <sup>0</sup> E <sup>‡</sup> ΔE	Fe <sup>II</sup> E <sup>‡</sup>	⇌ Fe <sup>III</sup> ΔE
Ferrocene			+471	55
3			+640	61
4	–205	86 <sup>b</sup>	+758	90 <sup>b</sup>

<sup>a</sup> Data in mV. Bu<sup>n</sup><sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> 0.1 mol dm<sup>-3</sup> in CH<sub>2</sub>Cl<sub>2</sub>, Pt electrode, 20 °C, scan rate 100 mv s<sup>-1</sup> vs. <sup>b</sup> No compensation for internal resistance of cell.

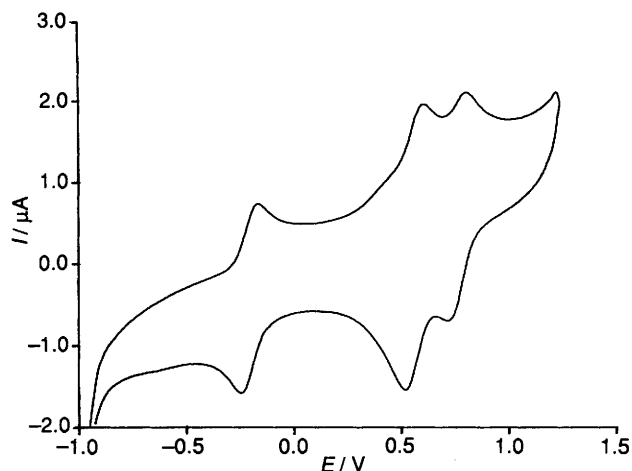


Fig. 2 Cyclic voltammogram of 4

the crystal structure (Fig. 1) is the non-planarity of the dithiole ring in relation to the cyclopentadienyl ring, the ligand being twisted by ca. 20° around the C(1)–C(4) axis. Sterically, this could be due to intramolecular interactions between H(1)–H(2) forcing the dithiole ring out of planarity, possibly hindering the potential stacking properties of the molecule.

The electrochemical properties of 4 have been studied by cyclic voltammetry (Fig. 2) and the comparative half-wave potentials for ferrocene and compounds 3 and 4 are shown in Table 1.

Compound 3 has a half-wave potential of 659 mV as compared to 482 mV for ferrocene. This shift in potential is due to the electron withdrawing effect of the ethenedithiolate substituent reducing electron density within the metallocene and making it more difficult to oxidise. On forming the nickel(II) complex of the ethenedithiolate ligand (complex 4), three reversible one electron oxidations are observed. The first and second oxidations can be assigned to redox processes located on the metal–ligand core:  $[ML_2]^{2-} \rightarrow [ML_2]^{-1}$  and  $[ML_2]^{-1} \rightarrow [ML_2]^0$ , respectively.<sup>8</sup> The third oxidation is assigned to the process: ferrocene  $\rightarrow$  ferrocinium, on the basis that the oxidation potential for 3 will be enhanced due to the greater electron withdrawing effect on the dithiolene core in 4. In complex 4 oxidation of the two ferrocene moieties occurs at the same potential, suggesting that the dithiolene core prevents communication between the ferrocene redox centres.

These studies are being extended to other bis(ferrocene ethenedithiolate)  $M^{II}$  complexes where  $M = Co, Cu$  and  $Au$ , and will be reported in due course.

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### Footnotes

† All new compounds gave satisfactory elemental analysis, and mass and <sup>1</sup>H NMR spectra.

‡ Sulfur and selenium analogues have been previously prepared (ref. 7).

§ Selected physical data for 4: dec. temp. >195 °C; NIR (CH<sub>2</sub>Cl<sub>2</sub>) λ = 1030 nm (ε ≈ 10 000 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) FAB-MS (m/z) 608; satisfactory elemental analyses (C, H) were obtained.

¶ Crystal data for 3: C<sub>13</sub>H<sub>10</sub>FeOS<sub>2</sub>, M = 302.19, monoclinic, space group P2<sub>1</sub>/a, a = 11.136(2), b = 7.568(2), c = 14.715(1) Å, β = 103.388(9)°, V = 1206.6(4) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.663 g cm<sup>-3</sup>, μ(Mo–Kα) = 15.58 cm<sup>-1</sup>, F(000) = 616. Data were collected at room temp. on a Rigaku AFC5R diffractometer using graphite-monochromated Mo–Kα radiation (λ = 0.71069 Å) and ω/2θ scan mode. The structure was solved by the Patterson Method. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares to give R = 0.037, R<sub>w</sub> = 0.039 for 1772 reflections with |F<sub>o</sub>| > 3σ(|F<sub>o</sub>|). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See notice to Authors, Issue No. 1.

|| By observing the relative shift of the ferrocenyl peaks in the <sup>1</sup>H NMR of 3 and 4.

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