

Bipyridyl podands in a 1,1'-disubstituted ferrocene

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Abstract

The reaction of disodium ferrocenedithiolate **1** with 6-bromomethyl-6'-methyl-2,2'-bipyridyl **2** gave 1,1'-bis(6-methanethio-6'-methyl-2,2'-bipyridyl)ferrocene **3** which was shown to form complexes with Ag^+ and Cu^+ by a combination of mass spectrometry, multinuclear NMR and cyclic voltammetry.

Keywords: Ferrocene; Bipyridyl; Podands; Ag^+ -complex; Cu^+ -complex

1. Introduction

Redox-active macrocycles and cryptands containing metallocene units have attracted considerable attention in recent years [1–3] especially since complexation with either cations or anions has been shown to alter the redox behaviour of the host molecule [4]. The early work in this area involved complexation with 'hard' cations (e.g. Na^+ , Ca^{2+} or Y^{3+}) [5], but as ligands containing nitrogen and sulphur derivatised with metallocenes were developed, the complexation studies were extended to 'soft' transition metal cations [6]. Apart from macrocyclic derivatives of metallocenes, the field also includes metallocenes functionalised with 1,1'-podand arms [7] which are less specific in terms of size complementarity but more flexible than their macrocyclic cryptand analogues. This paper reports the synthesis of a novel 1,1'-bis(bipyridyl) derivative of ferrocene **3** (see Fig. 1) and its complex formation with Ag^+ and Cu^+ cations.

2. Experimental

^1H and ^{13}C NMR spectra were recorded on either Bruker AM360 or Bruker WX400 spectrometers using CDCl_3 or CD_3CN as solvents. Mass spectra were obtained using FAB with a thioglycerol matrix on a Kratos

MS890MS instrument at the ULIRS Mass Spectrometry Service, King's College, London. UV spectra were recorded on a Hewlett-Packard Diode Array Spectrometer (Model no. 8452A) using 1 mm and 10 mm path length quartz cuvettes. Cyclic voltammograms were recorded at 293 K using an EG&G Model 273 potentiostat with Model 270 software controlled by a Vigen computer connected to a Hewlett-Packard colour plotter for graphical output. The cyclic voltammetry experiments were conducted in dry, nitrogen-purged CH_3CN with 0.1 M Bu_4NClO_4 as supporting electrolyte, using Ag/AgNO_3 (0.01 M) in acetonitrile as the reference electrode [8] and Pt wire as both counter and working electrodes. The scan rate was normally 100mVs^{-1} with IR compensation applied during each scan.

2.1. Preparative details

Ferrocene-1,1'-dithiol **1** and 6-bromomethyl-6'-methyl-2,2'-bipyridyl **2** were prepared according to literature procedures [9,10].

2.2. Synthesis of 1,1'-bis(6-methanethio-6'-methyl-2,2'-bipyridyl)ferrocene **3**

A degassed solution of aqueous sodium hydroxide (0.4 ml, 20%) was added under nitrogen to a solution of ferrocene-1,1'-dithiol **1** (85 mg, 0.34 mmol) in degassed absolute ethanol (5 ml). A solution of 6-bromomethyl-6'-methyl-2,2'-bipyridyl **2** (180 mg, 0.68 mmol) in ethanol (15 ml) was added dropwise to the stirred sodium

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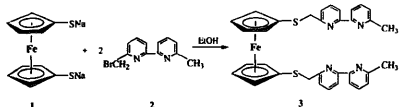


Fig. 1.

ferrocene dithiolate and the mixture was stirred at room temperature for a further 24 h. Evaporation of the solvent gave a brown residue which was dissolved in water (80 ml) and extracted with diethyl ether (3 × 30 ml). The organic layer was dried (MgSO₄) and chromatographed on silica. Elution with CH₂Cl₂–1% MeOH gave a yellow band from which the ligand (40 mg, 20%) was isolated as a yellow solid, m.p. 80–85°C, MS/FAB (M + 1) = 615; exact mass FAB: 615.1320; calculated for C₃₄H₃₁S₂N₄Fe: 615.1340. Several attempts at elemental analysis resulted in found values for C, H and N which were in the correct ratio (C₃₄H₃₀N₄) but the absolute values were not acceptable. The reason for this anomaly is unknown.

¹H NMR (CDCl₃): δ 2.61 (s, 6H, CH₃), 3.96 (s, 4H, CH₂), 4.15 (m, 4H, Fe–H), 4.17 (m, 4H, Fe–H), 7.11 (m, 4H), 7.65 (m, 4H), 8.09 (d, 2H, J = 7.9 Hz), 8.21 (d, 2H, J = 7.9 Hz) all due to the bipyridyl hydrogens.

¹³C NMR (CDCl₃): δ 24.6 (CH₃), 44.1 (CH₂), 70.8, 74.9, 80.3 (ipso- all cp carbons), 118.4, 119.1, 122.9, 123.1, 136.9, 137.1, 155.5 (ipso), 155.9 (ipso), 157.7 (ipso), 157.7 (ipso). Very similar, but not so well-re-

solved, shifts were observed in CDCl₃–CD₃CN. UV (CH₃CN), λ_{max} (nm): 200, 240, 292 and 440 (ε = 260 dm³ mol⁻¹ cm⁻¹).

2.3. Complex formation of 3 with Ag⁺

A mixture of 3 (2.3 mg, 3.7 × 10⁻³ mmol) with AgBF₄ (0.7 mg, 3.6 × 10⁻³ mmol) in acetonitrile (10 ml) was stirred in the dark for 24 h. Diethyl ether (50 ml) was added slowly to the mixture until yellow flakes precipitated, which were filtered, washed with diethyl ether and dried under vacuum at room temperature to give 3 mg (75% yield) of the 1:1 complex of AgBF₄ with 3, m.p.: 190–195°C, MS/FAB (3 + AgBF₄ + 4H₂O) = 882; UV (CH₃CN), λ_{max} (nm): 196, 246 and 302.

2.4. Complex formation of 3 with Cu⁺

Cuprous(tetrakisacetonitrile)tetrafluoroborate, Cu(CH₃CN)₄BF₄, was prepared by heating a mixture of NaBF₄ (5 g, 45 mmol), CuSO₄ · 5H₂O (5.7 g, 23 mmol) and copper powder (1.45 g, 23 mmol) in CH₃CN (150 ml) for 6 h. The product (4.1 g, 57%, exact mass FAB 314.0389; calculated for C₈H₁₂N₄BF₄Cu 314.0387) was recrystallized from acetonitrile under nitrogen [11].

A solution of 3 (5.5 mg, 8.9 × 10⁻³ mmol) and Cu(CH₃CN)₄BF₄ (2.8 mg, 8.9 × 10⁻³ mmol) in acetonitrile–dichloromethane (10 ml, 1:1) was stirred at room temperature for 24 h. Diethyl ether (50 ml) was added

Table 1
¹H NMR of 3 and 1:1 complexes with Ag⁺ and Cu⁺ in acetonitrile-d₃ at 293 K

Assignment	CH ₃	CH ₂	H _{α,α'}	H _{β,β'}	H ¹⁻⁵ , H ^{3-5'}
3 δ (ppm)	2.54 (s, 6H)	3.93 (s, 4H)		4.12 (m, 8H)	7.15 (m, 2H), 7.68 (m, 2H), 8.05 (d, 1H, J = 7.7 Hz), 8.19 (d, 1H, J = 7.8 Hz)
3:AgBF ₄ δ (ppm)	2.44 (s, 6H)	3.66 (t, 4H)	3.97 (s, 4H)	4.13 (t, 4H, J = 1.8 Hz)	7.33 (d, 1H, J = 7.1 Hz), 7.44 (d, 1H, J = 7.5 Hz), 7.95 (tt, 2H), 8.17 (dd, 2H)
3:CuBF ₄ δ (ppm)	2.08 (s, 6H)			4.15 (br, 12H)	7.49 (d, 1H, J = 7.7 Hz), 7.62 (d, 1H, J = 7.7 Hz), 8.05 (tt, 2H), 8.36 (dd, 2H)

Table 2
¹³C NMR of 3 and 1:1 complexes with Ag⁺ and Cu⁺ in acetonitrile-d₃ at 293 K

Assignment	CH ₃	CH ₂	C _{α,α'} , C _{β,β'}	C ₁	C ¹⁻⁵ , C ^{3-5'}	C ^{2,6} , C ^{2',6'}
3 δ (ppm) (CD ₃ CN/CDCl ₃)	24.6	44.0	71.1, 75.1	76.3	118.5, 119.4, 123.6, 123.8, 137.7, 137.8	158.3, 158.6
3:AgBF ₄ δ (ppm)	25.9	43.7	71.2, 75.1	87.6	121.2, 122.2, 126.3, 126.8, 139.9, 140.2	ψ
3:CuBF ₄ δ (ppm)	24.9	43.8	74.4, 74.3	82.8	120.7, 121.5, 126.9, 127.1, 139.3, 139.4	152.3, 153.3, 158.0, 159.8

ψ not observed.

slowly and the resulting orange precipitate was filtered, washed with diethyl ether and dried under vacuum to give 3 mg (40% yield) of the red complex, which decomposed before melting. MS/FAB ($3 + \text{Cu}^+$) =

678; UV (CH_3CN), λ_{max} (nm): 194, 250, 304 and 456 ($\epsilon = 6200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

^1H NMR data of the complexes of **3** with Ag^+ and Cu^+ are recorded in Table 1 and ^{13}C data in Table 2.

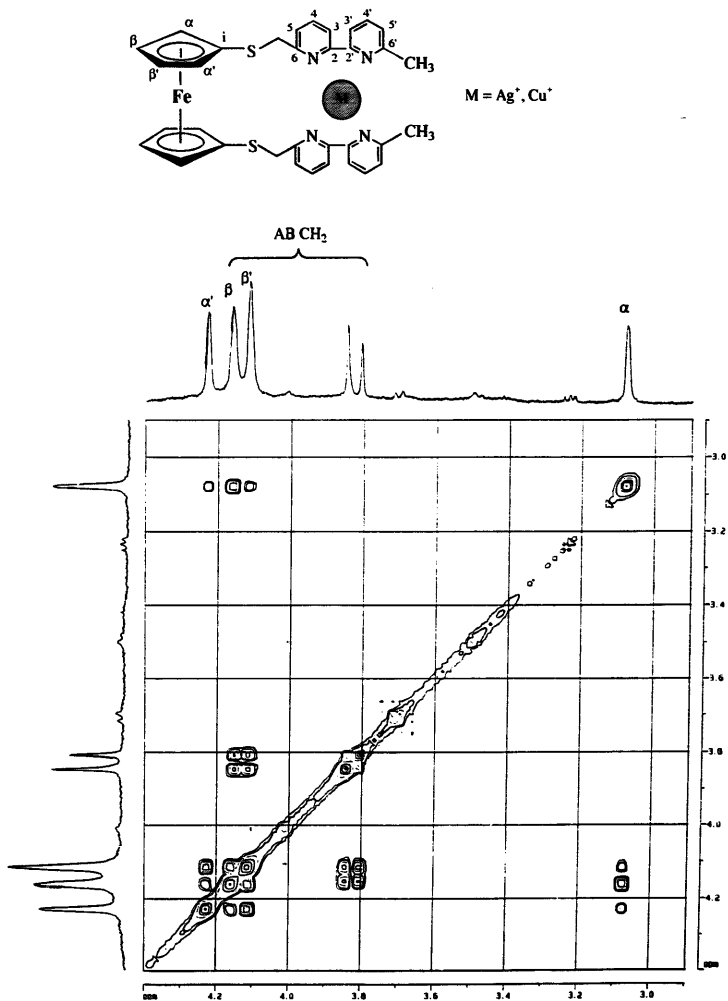


Fig. 2. Atom numbering scheme and COSY 45 at 233 K of **3**:CuBEt₃.

3. Results and discussion

The proton NMR spectra of the ligand **3** is significantly different from those of the Ag^+ and Cu^+ complexes. The bipyridyl protons shift somewhat erratically but the cp, CH_2 and CH_3 protons all move upfield slightly on complexation with Ag^+ . With Cu^+ the methyl protons again move upfield but the CH_2 and cp protons merge into a broad, unresolved resonance around 4.14 ppm which suggests a dynamic process within the molecule (vide infra).

Variable-temperature ^1H NMR spectra (Table 3) showed that the dynamic process within the Cu^+ complex is slow on the NMR time scale below 293 K. The CH_2 signal resolved into an AB quartet at low temperature; similar behaviour has been found for the bipyridine resonances in Cu(I) oligobipyridines [12]. A COSY 45 experiment at 233 K assigned the AB quartet buried beneath the β and β' ferrocene peaks (Fig. 2) and a coupling constant $J_{\text{AB}} = 15.1$ Hz was determined for the quartet. The prochirality of the methylene groups at 233 K is consistent with tetrahedral coordination of Cu(I) by the bipyridyl units. Both ferrocene proton pairs also became non-equivalent; the α ferrocene signal was shifted upfield by more than 1 ppm to 3.06 ppm, whereas the α' -proton was found at 4.21 ppm. This indicates a slow exchange process with a coalescence temperature around 293 K for all three processes and a value of $\Delta G^\ddagger = 55\text{--}60$ kJ mol $^{-1}$ ($k_c = 270$ s $^{-1}$) was estimated for the process. Raising the temperature resolved the spectra into a pattern which was very similar to that found for the Ag^+ complex, where both α -protons of the cyclopentadiene ring were shifted to higher field. Such behaviour implies that the Cu(I) ion has access to more than one coordination geometry on the NMR time scale and there is still a very fast exchange process between ligand-coordinated and solvated forms of the copper ion. The bipyridyl resonances do not change drastically over the temperature range except for protons (5 and 5') next to the substituents, which are shifted slightly at higher temperature. This suggests that

Table 3
Variable-temperature ^1H NMR of 3:CuBF_4 in acetonitrile- d_3 ^a

T (K)	CH_3	H_α	CH_2	H_β	H_β	H_α'
335	2.09 s	3.71 br	4.05 s		4.16 s	
327	2.09 s	3.74 br	4.04 s		4.16 s	
318	2.09 s	3.75 br	4.03 s		4.16 s	
310	2.11 s	3.77 br	4.01 br		4.15 s	
293	2.07 s			4.14 br		
283	2.05 s	3.09 br	3.84 br		4.14 br, sh	
273	2.04 s	3.08 s	3.80 s, 3.84 s	4.11 s	4.16 s	4.22 s
263	2.02 s	3.06 s	3.79 s, 3.83 s	4.10 s	4.15 s	4.21 s
253	2.03 s	3.07 s	3.79 s, 3.84 s	4.11 s	4.16 s	4.22 s
233	2.01 s	3.06 s	3.79 s, 3.83 s	4.09 s	4.14 s	4.21 s

^a $\text{H}^{5,5'}$, $\text{H}^{4,4'}$ and $\text{H}^{3,3'}$ gave virtually identical signals over the whole temperature range (see Table 1).

Table 4

Redox potentials (vs. Ag/AgNO_3) and peak separation in acetonitrile^a at 293 K

	$E_{1/2}$ (V)	ΔE (mV)
3	0.12	78
3 : AgBF_4	0.23	136
3 : CuBF_4	0.20, 0.47	92, 106
$\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$	0.76	180
Ferrocene	0.13	84

^a Conc.: **3**, 2.44×10^{-3} M; **3**: AgBF_4 , 0.5×10^{-3} M; **3**: CuBF_4 , 1.65×10^{-3} M, others 5×10^{-3} M.

both the Cu(I) and Ag(I) ions are strongly coordinated at the bipyridyl site of the ligand.

The electronic spectrum of the intense orange solution of the Cu(I) complex exhibits a strong absorption ($\lambda_{\text{max}} = 456$ nm, $\epsilon = 6200$ dm 3 mol $^{-1}$ cm $^{-1}$) bathochromically shifted relative to **3** which is analogous to $[\text{Cu}(\text{bipy})_2]^+$ complexes [13].

The redox potentials of the ligand and its complexes were investigated by cyclic voltammetry and the data are summarised in Table 4. The complexes were studied in their isolated form and were also generated in situ by complexation of the ligand using AgBF_4 and $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ in acetonitrile to confirm the ligand/metal stoichiometry.

The ligand exhibited a reversible redox wave at 0.12 V vs. Ag/AgNO_3 with a peak separation (78 mV) close to that observed for ferrocene (84 mV) under identical experimental conditions. Complexation with Ag^+ caused an anodic shift of 110 mV and the redox wave became quasi-reversible ($\Delta E = 136$ mV) although a plot of I_{pa} vs. (scan rate) $^{1/2}$ was linear. The Cu^+ complex was oxidized in two quasi-reversible one-electron steps (Fig. 3) due to the FeII/FeIII redox couple ($E_{1/2} \sim 0.2$ V) and the CuI/CuII couple ($E_{1/2} \sim 0.47$ V) both of which showed linear I_{pa} vs. (scan rate) $^{1/2}$ plots. The cathodic shift (290 mV) associated with the CuI/CuII redox couple clearly indicates increased electron density on the bound cation. The redox potential is similar to those found for Cu(I) ions com-

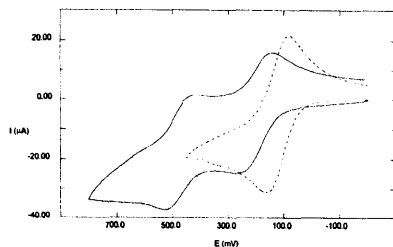


Fig. 3. Cyclic voltammograms recorded at a platinum electrode in acetonitrile containing 0.1 M NBu_4ClO_4 : **3** (—); **3**: CuBF_4 (---); **3**: AgBF_4 (· · ·).

plexed by substituted 1,10-phenanthroline ligands which possess a pseudotetrahedral coordination geometry [14]. No change was observed when the cyclic voltammograms were recorded at lower temperatures.

4. Conclusions

1,1'-Bis(6-methanethio-6'-methyl-2,2'-bipyridyl)ferrocene **3** forms 1:1 stoichiometric complexes with Ag⁺ and Cu⁺ ions. The ferrocene-centred redox potential shifted anodically after complexation (ca. 100 mV) while the cathodic shift of the CuI/CuII couple confirmed a pseudotetrahedral coordination geometry.

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