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Redox-active Schiff base ligands

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Abstract

The syntheses and characterisation of two redox-active Schiff base ligands containing ferrocene are described, and their complex formation with Cu^+ and Ag^+ examined by UV/vis and ^1H-, ^{13}C-NMR spectroscopy, cyclic voltammetry and X-ray crystallography. Crystals of the complex formed between bis-(3-ethylenedi-imino-4-methoxyphenyl)ferrocene and $AgBF_4$ belong to the highly unusual cubic system and spontaneous resolution of the helical, tetrahedral complex is observed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Schiff base; Ferrocene; Ag^+-complex; Cu^+-complex; X-ray crystallography

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1. Introduction

During the last 10 years a considerable number of redox-active macrocycles and cryptands, containing either metallocene or quinone units, have been synthesised and their complex formation with both anionic and cationic guests investigated [1]. More recently however, the field has been extended to include a variety of coordinating ligands containing sulphur or nitrogen attached to the metallocene unit [2,3]. These molecules also behave as hosts to cationic guests and with this, and the possibility of binuclear complexes as catalysts [4] in mind, it was decided to attempt the synthesis of ligands of type **1** that might afford binuclear complexes of type **2**, and therefore possible catalysts for the oxidation of water [5]. This paper reports the outcome of this work, which led to an unusual crystal structure for a Ag^+-complex.

2. Experimental

All reactions were carried out using anhydrous solvents unless otherwise stated. The solvents were dried by the usual procedures and stored under dinitrogen gas atmosphere and over activated molecular sieves. Chromatography columns were packed using Kieselgel 60 (70-230 mesh) or aluminium oxide type 507C neutral (100-125 mesh). ^1H- and ^{13}C-NMR spectra were recorded on either Bruker AM360 or Bruker AMX400 spectrometers. ^1H-NMR spectra were referenced to TMS as internal standard and ^{13}C-NMR spectra were referenced to the solvent signal at 77 ppm in $CDCl_3$ and 1.3 ppm in CD_3CN. ^{13}C-DEPT spectra were recorded using the 135° pulse sequence, giving positive signals for CH_3 and CH, negative signals for CH_2 and no signal for quaternary (*ipso*) carbon atoms. MS spectra were obtained using FAB with a thioglycerol or 3-NBA matrix on a Kratos MS890MS instrument at the ULIRS Mass Spectrometry Service, King's College, London. Exact mass was determined by the chemical ionisation technique. UV spectra were recorded on a Hewlett-Packard diode array spectrometer (Model no. 8452A) using 1 and 10 mm path length quartz cuvettes. IR spectra were recorded as KBr discs using a FT-IR

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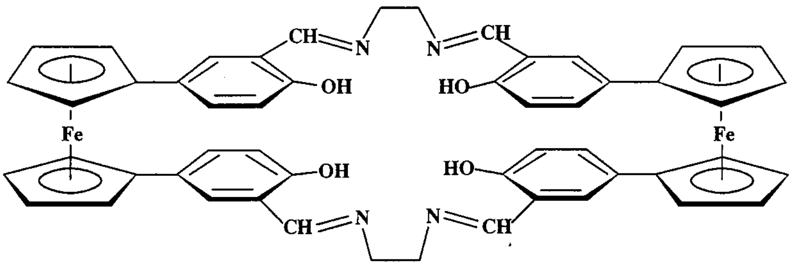

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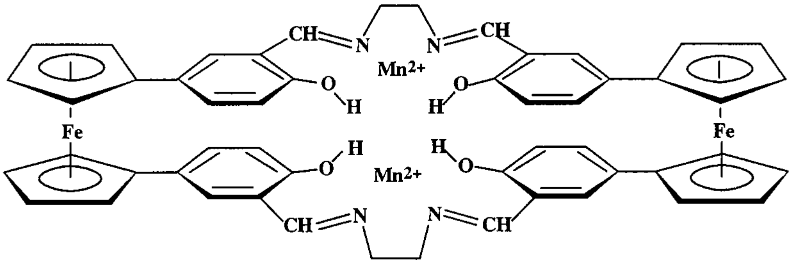

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Scheme 1. The synthesis of suitable ferrocene derivatives to allow a Schiff condensation with α,ω-diamines.

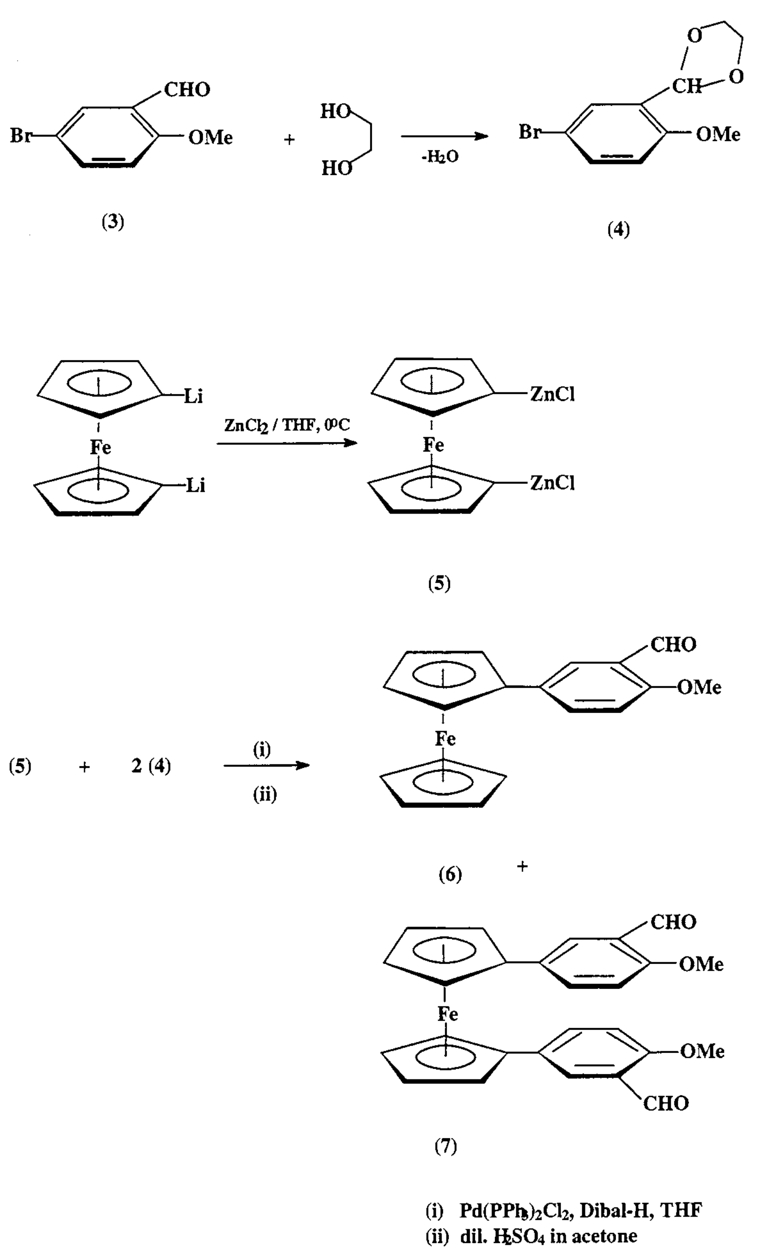
spectrometer (Model 1605). Cyclic voltammograms were recorded at 293 K using an EG&G Model 273 potentiostat with Model 270 software controlled by a Viglen computer connected to a Hewlett-Packard Colour Plotter for graphical output. The cyclic voltammetry experiments were conducted in dry, nitrogen-purged CH_3CN with 0.1 M Bu_4NClO_4 or dry, nitrogen-purged CH_2Cl_2 with 0.4 M Bu_4NClO_4 as supporting electrolyte, Ag/AgCl (sat. AgCl in 3 M NaCl) or $Ag/AgNO_3$ (0.01 M in acetonitrile) as the reference electrode and Pt wire as both counter and working electrode. The scan rate was normally 100 mV s^{-1} with IR compensation applied during each scan.

2.1. *Crystal data for the complex of **9** with Ag(I)*

Orange prismatic crystals were prepared by slow evaporation of a dichloromethane solution of the compound and mounted on a thin glass fibre using a fast setting epoxy resin. A total of 90 oscillation frames of 45 s exposure time each with 2° rotation in ϕ were recorded using a Nonius Kappa CCD diffractometer, with a detector-to-crystal distance of 25 mm. The crystal was indexed from the first ten frames using the DENZO package [6] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling of the whole data set resulted in a total of 3517 unique data corrected for Lorentz and polarisation effects and for absorption using the programme Scalepack [6], which were used in subsequent refinement. The structure was solved using the direct methods option of SHELXS-97 [7] and developed via alternating least-squares cycles and difference Fourier synthesis (SHELXL-97) [7]. All non-hydrogen atoms were modelled anisotropically, except those of one disordered component of the tetrafluoroborate anion. Hydrogen atoms were placed in calculated positions, assigned as an isotropic thermal parameter 1.2 times that of the parent atom and allowed to ride on the atom to which they were attached. The tetrafluoroborate anion was found to exist in two possible sites each of 50% occupancy, situated upon the four-fold axis. Refinement converged with $wR_2 = 0.1626$ for data with $2\theta \leq 50°$, which corresponds to a conventional R-factor of 0.0582 for data with $I > 2\sigma(I)$.

2.2. *Synthesis of 5-bromo-o-anisaldehyde ethylene acetal (**4**)*

5-Bromo-*o*-anisaldehyde (**3**, 10 g, 46.5 mmol), ethylene glycol (3.46 g, 55.8 mmol) and *p*-toluenesulphonic acid (0.884 g, 4.65 mmol) were heated under reflux in toluene (200 ml) in a Dean–Stark apparatus until 2.5 ml water separated. After cooling to r.t., the mixture was treated with solid sodium carbonate until the pH became neutral and stirred for 1 h. The organic solution was then washed several times with H_2O and dried over K_2CO_3. Evaporation of the solvent yielded an orange oil (7.78 g, 65%); MS, CI/high resolution:

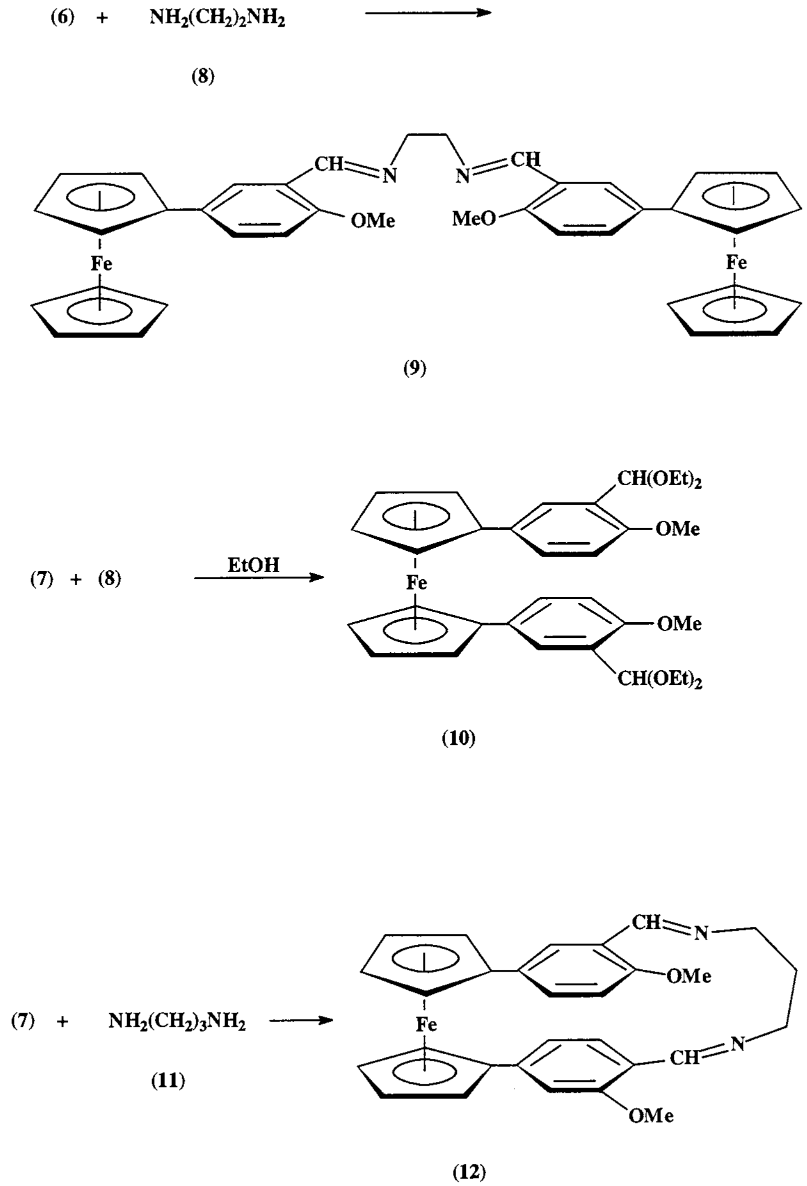


Scheme 1. (*Continued*)

$(C_{10}H_{11})_3Br$. calc. 257.9892 and 259.9872; found 257.9888 and 259.9887). ^1H ($CDCl_3$): 3.81 (m, 3H), 3.99 (m, 2H), 4.10 (m, 2H), 6.08 (s, 1H), 6.74 (d, 1H), 7.39 (dd, 1H), 7.63 (d, 1H). ^{13}C ($CDCl_3$): 55.8 (CH_3), 65.3 (CH_2), 98.5, 112.5 (both CH), 112.8, 128.0 (both C), 129.6, 132.8 (CH), 156.7 (C).

2.3. Synthesis of 1,1′-bis(o-anisaldehyde ethylene acetal)ferrocene and (o-anisaldehyde ethylene acetal)ferrocene

A mixture of ferrocene (2 g, 10.7 mmol) in diethylether (40 ml) was added to a mixture of TMEDA (9.6 ml, 24 mmol) and *n*-BuLi (3.62 ml, 24 mmol) in diethylether (10 ml) at r.t. The solution was stirred for 12 h when an orange precipitate formed. A cooled solution of dried $ZnCl_2$ (2.93 g, 21.5 mmol) in THF (10 ml) was added to the stirred suspension at 0°C and stirred for 1 h to give **5**. In a separate flask, $Pd(PPh_3)_2Cl_2$ [8] (351 mg, 0.5 mmol) was suspended in THF (20 ml), to which Diabal-H® (di-isobutylalumium hydride), (1 M in hexane, 1.05 ml) was added dropwise. This gave a homogenous dark solution of $Pd(PPh_3)_2$ that was added to the 1,1′-bis(zinc chloride)ferrocene via a cannula. 5-Bromo-*o*-anisaldehyde ethylene acetal (6.96 g, 26.9 mmol) was dissolved in THF (20 ml) and added to the reaction mixture. The suspension was stirred for 24 h until the brown solution became clear



Scheme 1. (*Continued*)

and was then heated under reflux for a further 24 h. An aqueous solution of NaOH (10% w/v, 80 ml) was added slowly to the mixture at r.t. The organic layer was separated, washed with H_2O and dried over $MgSO_4$. The residue was chromatographed on silica (orange–yellow band) to give the monosubstituted ferrocene by elution with hexane/dichloromethane (3:2) as an orange solid, m.p. 100–105°C, MS: EI 364.0738 calculated for $C_{20}H_{20}O_3Fe = 364.0761$. ^1H ($CDCl_3$): 3.86 (s, 3H, OCH_3), 4.03 (s, 5H, fc), 4.15 (br, 4H), 4.27 (s, 2H), 4.60 (s, 2H), 6.15 (s, 1H), 6.83 (d, 1H, $J = 8.3$ Hz), 7.42 (d, 1H, $J = 7.7$ Hz), 7.61 (s, 1H). ^{13}C ($CDCl_3$): 55.6 (OCH_3), 65.2 (CH_2), 66.3 (fc), 68.5 (fc), 69.5 (unsubst fc), 86.0 (*ipso*), 99.3 (CH), 124.4 (CH), 125.4 (C), 127.8 (CH), 131.0 (C), 156.0 (*ipso*). 1,1′-Bis(*o*-anisaldehyde ethylene acetal)ferrocene was obtained as a red band by elution with dichloromethane–1% methanol and after evaporation of the solvent as red crystals (2.36 g, 41%), m.p. 160–165°C (dec). RMM:FAB 542 (M, 100%), 543 (M + 1, 74%), 544 (M + 2, 27%); ^1H ($CDCl_3$): 3.84 (s, 3H), 4.02 (s, 2H), 4.13 (s, 2H), 4.17 (s, 2H), 4.47 (s, 2H), 6.11 (s, 1H), 6.67 (d, 1H, $J = 8.1$ Hz), 7.11 (d, 1H, $J = 7.8$ Hz), 7.46 (s, 1H). ^{13}C ($CDCl_3$): 55.4 (OCH_3), 65.1 (CH_2), 67.2 (fc), 70.0 (fc), 87.0 (*ipso*), 99.3 (CH), 110.5 (CH), 124.1 (CH), 125.0 (C), 127.7 (CH), 129.4 (C), 155.9 (C).

2.4. *Synthesis of 3-formyl-4-methoxyphenyl-ferrocene (6)*

(*o*-Anisaldehyde ethylene acetal)ferrocene was dissolved in acetone (50 ml) and heated under reflux for 10

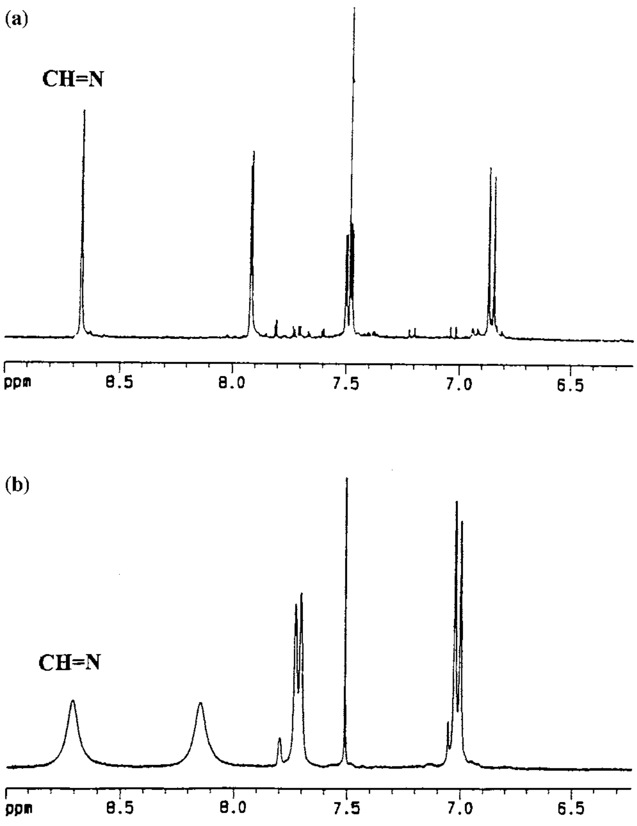


Fig. 1. ^{1}H spectra of (a) ligand **9** and (b) the $CuBF_4$ complex

min in the presence of conc. H_2SO_4 (20 mg). The reaction mixture was neutralised with Na_2CO_3, filtered and evaporated to give an orange, oily residue. The product was recrystallised from acetone, precipitated with hexane and washed with diethylether to yield a yellow solid (0.75 g, 22%), m.p. 105–108°C. RMM (CI) *m*/*z* 320.05 (100%): exact mass FAB/MS; found, 320.0513: calculated for $C_{18}H_{16}O_2Fe$, 320.0499. ^{1}H ($CDCl_3$); 3.93 (s, 3H), 4.02 (s, 5H, cp), 4.30 (br, 2H, fc), 4.62 (br, 2H, fc), 6.93 (dd, 1H, $J = 8.7$ Hz), 7.65 (d, 1H, $J = 8.6$ Hz), 7.91 (d, 1H, $J = 2.3$ Hz). ^{13}C ($CDCl_3$): 55.7 (OCH_3), 66.1 (fc), 68.9 (fc), 69.5 (unsubst fc), 84.1 (*ipso*), 111.8 (CH), 124.5 (C), 131.8 (C), 133.3 (CH), 160.2 (*ipso*), 189.8 (CH).

*2.5. Synthesis of bis-(3-ethylenediimine-4-methoxyphenyl)ferrocene (**9**)*

3-Formyl-4-methoxyphenylferrocene (**6**, 90 mg, 2.81×10^{-4} mol) in ethanol (5 ml) was heated under reflux and 1,2-diaminoethane (5.5 mg, 2.8×10^{-4} mol) was added slowly to the mixture, which was heated under reflux for a further 30 min. Evaporation of the solvent under high vacuum (0.2 mmHg) gave an orange yellow crystalline solid, which was recrystallised from dichloromethane to give an orange solid (90 mg, 95%), m.p. 55–58°C, RMM:FAB 665 (M + 1). Calculated for $C_{39}H_{36}N_2O_2Fe_2.0.5CH_2Cl_2$: C 65.42, H 5.28, N 3.96; found, C 65.29, H 5.56, N 3.52. UV (CH_2Cl_2): $\lambda = 242$, 286, 328, 450 nm. ^{1}H ($CDCl_3$): 3.76 (s, 6H), 3.99 (s, 10H), 4.03 (s, 4H) 4.25 (t, 4H), 4.62 (t, 4H), 6.79 d, 2H, $J = 8.6$ Hz) 7.47 (dd, 2H, $J = 8.5$ Hz), 8.00 (d, 2H, $J = 2.3$ Hz), 8.72 (s, 2H).^{13}C ($CDCl_3$): 55.5 (OCH_3), 62.0 (CH_2), 66.3 (fc), 68.5 (fc), 69.4 (unsubst fc), 85.2 (*ipso*), 111.0 (CH), 124.5 (C), 124.6 (CH), 129.4 (CH), 131.4 (C), 157.2 (C), 158.7 (CH).

*2.6. Attempted condensation of (**7**) with 1,2-diaminoethane*

1,1′-Bis(3-formyl-4-methoxyphenyl)ferrocene (7, 0.12 g, 2.81×10^{-4} mol) in ethanol (20 ml) was heated under reflux and 1,2-diaminoethane (16.9 mg, 0.0187 ml, 2.81×10^{-4} mol) in ethanol (5 ml) was added slowly over a period of 4 h. Evaporation of the solvent and drying gave an orange oil, which was characterised as 1,1′-bis(3-formyl diethylacetal-4-methoxyphenyl) ferrocene. ^{1}H ($CDCl_3$): 1.27 (m, 6H), 3.60 (m, 2H), 3.70 (m, 2H), 3.82 (s, 6H), 4.11 (s, 2H), 4.46 (s, 2H), 5.75 (s, 1H), 6.68 (d, 1H, $J = 8.5$ Hz), 7.15 (d, 1H, $J = 8.5$ Hz), 7.61 (s, 1H). ^{13}C ($CDCl_3$): 15.2 (CH_3), 55.4 (OCH_3), 62.1 (CH_2), 67.2 (fc), 70.2 (fc), 86.6 (*ipso*), 97.3 (CH), 110.6 (CH), 124.8 (CH), 126.7 (C), 127.0 (CH), 129.8 (C) 155.5 (C).

Table 1
The ^{1}H-NMR spectra of **9** and complexes with $CuBF_4$ and $AgBF_4$

	OCH_3	CH_2	cp	$H_{\alpha,\beta}$	H_{ϕ}	CH=N
δ (ppm)[a]	3.76 (s)	4.03 (s)	3.99 (s)	4.25 (t), 4.62 (t)	6.79 (d, $J = 8.6$Hz), 7.47 (dd, $J = 8.5$Hz), 8.00 (d, $J = 2.3$Hz)	8.72 (s)
$CuBF_4$ δ (ppm)[b]	3.91 (s)	3.62 (br)	4.02 (s)	4.31 (s), 4.61 (s)	7.03 (d, $J = 8.6$Hz), 7.74 (d, $J = 8.3$Hz), 8.17 (br)	8.73 (br)
$AgBF_4$ δ (ppm)[c]	3.87 (s)	3.39 (br)	3.96 (s)	4.23 (s), 4.43 (s)	6.92 (d, $J = 8.7$Hz), 7.66 (dd, $J = 8.7$Hz), 7.80 (d, $J = 2.2$Hz)	8.61 (s)

[a] Recorded in $CDCl_3$.

[b] Recorded in CD_3CN:$CDCl_3$ (1:1).

[c] Recorded in CD_3CN:$CDCl_3$ (1:4).

Table 2
The ^{13}C-NMR spectra of **9** and complexes with $CuBF_4$ and $AgBF_4$

	OCH_3	CH_2	$C_{\alpha,\beta}$, cp	C_{ι}	C_{ϕ}	C_{imino}
δ(ppm)[a]	55.5	62.0	66.3, 68.5, 69.4 (cp)	85.2	111.0 (CH), 124.5 (C), 124.6 (CH), 129.4 (CH), 131.4 (C), 157.2 (C)	158.7
$CuBF_4$ δ (ppm)[b]	56.4	62.0	66.7, 69.6, 70.1 (cp)	85.5	112.5 (CH), 125.1 (CH), 131.8 (C), 132.2 (CH), 158.4 (C)	160.6
$AgBF_4$ δ (ppm)[c]	57.2	62.9	68.0, 70.3, 71.0 (cp)	86.7	112.3 (CH), 124.2 (C), 124.5 (CH), 133.0 (CH),133.5 (C), 159.2 (C)	163.6

[a] Recorded in $CDCl_3$.
[b] Recorded in CD_3CN:$CDCl_3$ (1:1).
[c] Recorded in CD_3CN:$CDCl_3$ (1:4).

*2.7. Synthesis of 1,1′-{bis(4-methoxy-3-propanyl-imino)phenyl}ferrocenophane (**12**)*

Potassium carbonate (61 mg, 4.4×10^{-4} mol) and manganous perchlorate hexahydrate (40 mg, 1.1×10^{-4} mol) were added to a solution of (7, 50 mg, 1.2×10^{-4} mol) in a 1:1 (v/v) mixture of degassed dichloromethane and methanol (40 ml). The mixture was stirred for 3 h at r.t. when the orange solution darkened. A solution of 1,3-diaminopropane (8.2 mg, 1.1×10^{-4} mol) in methanol (5 ml) was then added and the resulting mixture was stirred at r.t. for 5 h. A dark precipitate was filtered off and the filtrate evaporated. The residue was recrystallized from methanol (0.5 ml) to give an orange precipitate (19 mg, 34%). m.p.:dec > 165°C. RMM:FAB 493 (M + 1); calculated for $C_{29}H_{28}N_2O_2Fe \cdot 4H_2O$: C 61.71, H 6.43, N 4.96; found C 60.69, H 5.97, N 4.97. ^{1}H ($CDCl_3$): 2.33 (m, 2H), 3.79 (s, 6H), 3.91 (m, 4H), 4.27 (t, 4H, $J = 1.9$ Hz), 4.57 (t, 4H, $J = 1.9$ Hz), 6.50 (d, 2H, $J = 8.6$ Hz), 7.01 (dd, 2H, $J = 8.6$ Hz), 7.72 (d, 2H, $J = 2.4$ Hz), 8.58 (s, 2H). ^{13}C ($CDCl_3$): 29.4 (CH_2), 55.5 (OCH_3), 63.6 (CH_2) 66.2 (fc), 68.6 (fc), 86.2 (*ipso*), 110.8 (CH), 124.3 (CH), 128.0 (C), 128.4 (CH), 157.0 (CH). A water peak was also in evidence.

2.8. Complexation of Schiff base ferrocene ligands

2.8.1. Bis(3-ethylenediimine-4-methoxyphenyl)ferrocene silver tetrafluoroborate

A stirred solution of bis(3-ethylenediimine-4-methoxyphenyl)ferrocene (9, 30 mg, 0.045 mmol) in degassed acetonitrile (20 ml) was treated with silver tetrafluoroborate (9 mg, 0.045 mmol) and the mixture was stirred overnight. Diethylether (100 ml) was then added to the yellow, cloudy solution and the precipitate formed was collected and dried as a yellow/brown powder, which was redissolved in dichloromethane/acetonitrile (4:1) and filtered twice. Evaporation gave orange crystals of the complex (20 mg, 53%). m.p. 105–110°C, RMM:FAB 753 (ligand + Ag). Calculated for $C_{38}H_{36}N_2O_2F_4BAgFe_2 + CH_3CN$: C 53.37, H 4.37, N 4.67; found, C 55.74, H 4.92, N 4.69. ^{1}H (CD_3CN:$CDCl_3$ 1:4): 3.39 (br, 2H), 3.87 (s, 3H), 3.96 (s, 5H), 4.23 (s, 2H), 4.43 (s, 2H), 6.92 (d, 1H, $J = 8.7$ Hz), 7.66 (dd, 1H, $J = 8.7$ Hz), 7.80 (d, 1H, $J = 2.2$ Hz), 8.61 (s, 1H). ^{13}C (CD_3CN:$CDCl_3$ 1:4): 57.2 (OCH_3), 62.9 (CH_2), 68.0 (fc), 71.0 (unsubst fc), 86.7 (*ipso*), 112.3 (CH), 124.2 (CH), 124.5 (CH), 133.0 (CH), 133.5 (C), 159.2 (C), 163.6 (CH).

2.8.2. Bis(3-ethylenediimino-4-methoxyphenyl)ferrocene copper tetrafluoroborate

A stirred solution of bis(3-ethylenediimino-4-methoxyphenyl)ferrocene (9, 51 mg, 7.7×10^{-3} mmol) in degassed acetonitrile (20 ml) was treated with cuprous[tetrakis(acetonitrile)]-tetrafluoroborate, $Cu(CH_3CN)_4BF_4$, (24 mg, 0.077 mmol) in acetonitrile and the mixture was stirred overnight. Diethylether (100 ml) was then added to the orange solution and a dark orange precipitate formed, which was collected and dried under vacuum (55 mg, 83%). m.p. 170–176°C (dec); RMM:FAB 857 (ligand + $CuBF_4$ + CH_3CN); IR 1623 cm^{-1}. Calculated for $C_{38}H_{36}N_2O_2F_4CuBFe_2 0.5CH_3CN.2H_2O$: C 53.76, H 4.80, N 4.02; found C 53.53, H 4.55, N 4.10. UV (CH_2Cl_2): λ, 240, 284, 334, 450 nm ($\varepsilon = 17760$ l mol^{-1} cm^{-1}). ^{1}H (CD_3CN/$CDCl_3$): 3.62 (br, 2H), 3.91 (s, 6H), 4.02 (s, 10H), 4.31 (s, 4H), 4.61 (s, 4H), 7.03 (d, 2H, $J = 8.6$ Hz), 7.74 (d, 2H, $J = 8.3$ Hz), 8.17 (br, 2H), 8.73(br, 2H). ^{13}C (CD_3CN/$CDCl_3$): 56.4 (OCH_3), 62.0 (CH_2), 66.7 (fc), 69.6 (fc), 70.1 (unsubst. fc), 85.5 (*ipso*), 112.5 (CH), 125.1 (CH), 131.8 (C), 132.2 (CH), 158.4 (C), 160.6 (CH). Water and acetonitrile were also evident in the ^{1}H-NMR spectrum.

*2.9. Complexation of 1,1′-{bis(4-methoxy-3-propanyl-imino)phenyl} ferrocenophane, **12**, by NMR*

2.9.1. 1,1′-{Bis(4-methoxy-3-propanyl-imino)phenyl}-ferrocenophane copper tetrafluoroborate

A mixture of 1,1′-{bis(4-methoxy-3-propanyl-imino)phenyl}ferrocenophane (10 mg, 10^{-5} mol) in

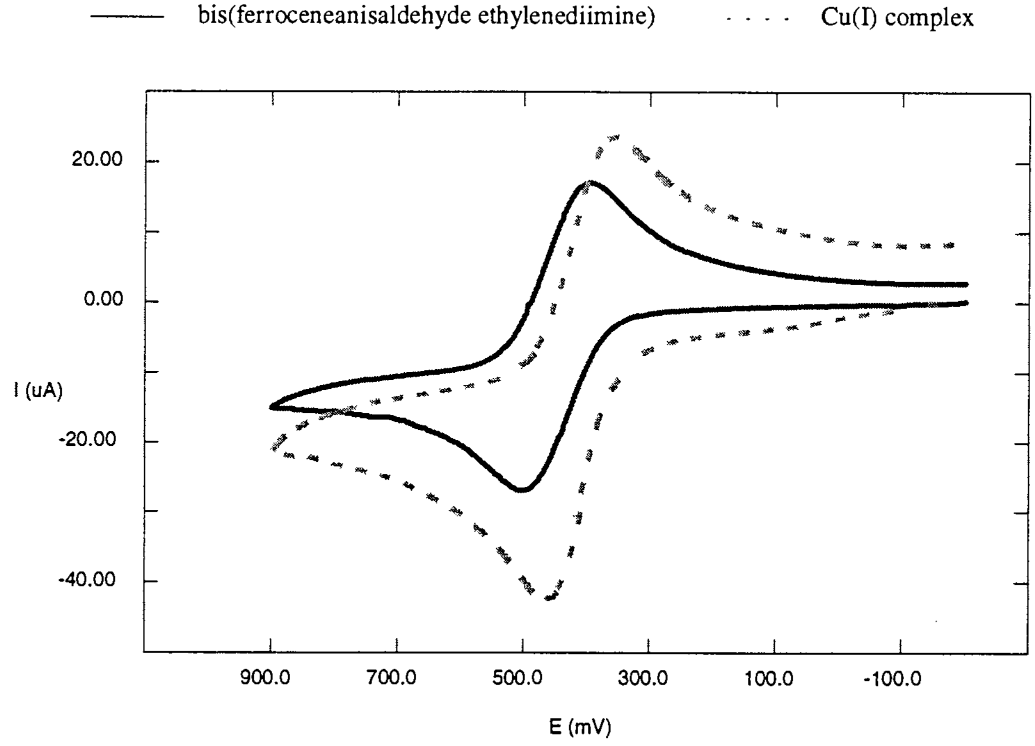


Fig. 2. The cyclic voltammogram of **9** and its Cu^+ complex in CH_2Cl_2 vs. Ag/AgCl

$CDCl_3$ (0.25 ml) and $Cu(CH_3CN)_4BF_4$ (3.2 mg, 10^{-5} mol) in CD_3CN (0.75 ml) was added to a nitrogen-purged NMR tube. ^1H ($CD_3CN:CDCl_3$ 3:1): 0.88 (br, 1H), 3.91 (s, 3H), 4.19 (br, 2H), 4.34 (br, 2H), 4.39 (br, 2H), 6.92 (d, 1H, $J = 8.6$ Hz), 7.52 (d, 1H, $J = 8.0$ Hz), 8.13 (s, 1H), 8.72 (s, 1H). ^{13}C ($CD_3CN:CDCl_3$ 3:1): 29.8 (CH_2), 32.4 (CH_2), 56.2 (OCH_3), 64.2 (CH_2), 68.0 (fc), 70.0 (fc), 112.1 (CH), 123.5 (CH), 131.4 (CH), 161.6 (CH). Reaction with an additional mole of copper caused the complex to precipitate and the product could not be redissolved in a variety of organic solvents.

2.9.2. *1,1′-{Bis(4-methoxy-3-propanyl-imino)phenyl}ferrocenophane silver tetrafluoroborate*

A mixture of 1,1′-{bis(4-methoxy-3-propanyl-imino)phenyl}ferrocenophane (5 mg, 5×10^{-6} mol) in $CDCl_3$ (0.5 ml) and $AgBF_4$ (2 mg, 5×10^{-6} mol) in CD_3CN (1 ml) was added to a nitrogen-purged NMR tube. The ^1H-NMR spectrum was very broad and could not be resolved at high or low temperature. The ^{13}C-NMR spectrum was recorded at r.t. by adjusting the acquisition parameters (PW = 4, AQ = 0.344 s). ^{13}C ($CD_3CN:CDCl_3$ 2:1): 29.7 (CH_2), 31.9 (CH_2), 55.6 (OCH_3), 63.9 (CH_2) 67.6 (fc), 109.4 (CH), 125.3 (CH), 132.9 (CH), 162.2 (CH).

3. Results and discussion

3.1. *Synthesis*

The first step was the synthesis of suitable ferrocene derivatives to allow a Schiff condensation with α,ω-diamines. This was achieved as shown in Scheme 1. Clearly the reaction proceeded in the expected manner but gave a mixture of mono- **6** and disubstituted **7** ferrocenes that were separated (at the aldehyde protected stage) by column chromatography on silica. Unfortunately, numerous attempts to demethylate **6** and **7** by all the known literature procedures [9] failed, and hence it was decided to prepare the Schiff base derivatives with **6** and **7**. Reaction of **6** with 1,2-ethylenediimine, **8**, gave the expected product, **9** in 95% yield. Reaction of **7** with **8** however, failed to give the expected product, but instead gave the diacetal **10**. This reaction is being investigated further in an attempt to avoid the readily formed acetal. One attempt to circumvent this involved the reaction of 1,3-diaminopropane, **11** with **7** which in fact gave a moderate yield (34%) of the cyclic diimine, **12**. Complexation of **9** and **12** with a range of cations was then explored and the results achieved with Cu^+ and Ag^+ are reported below.

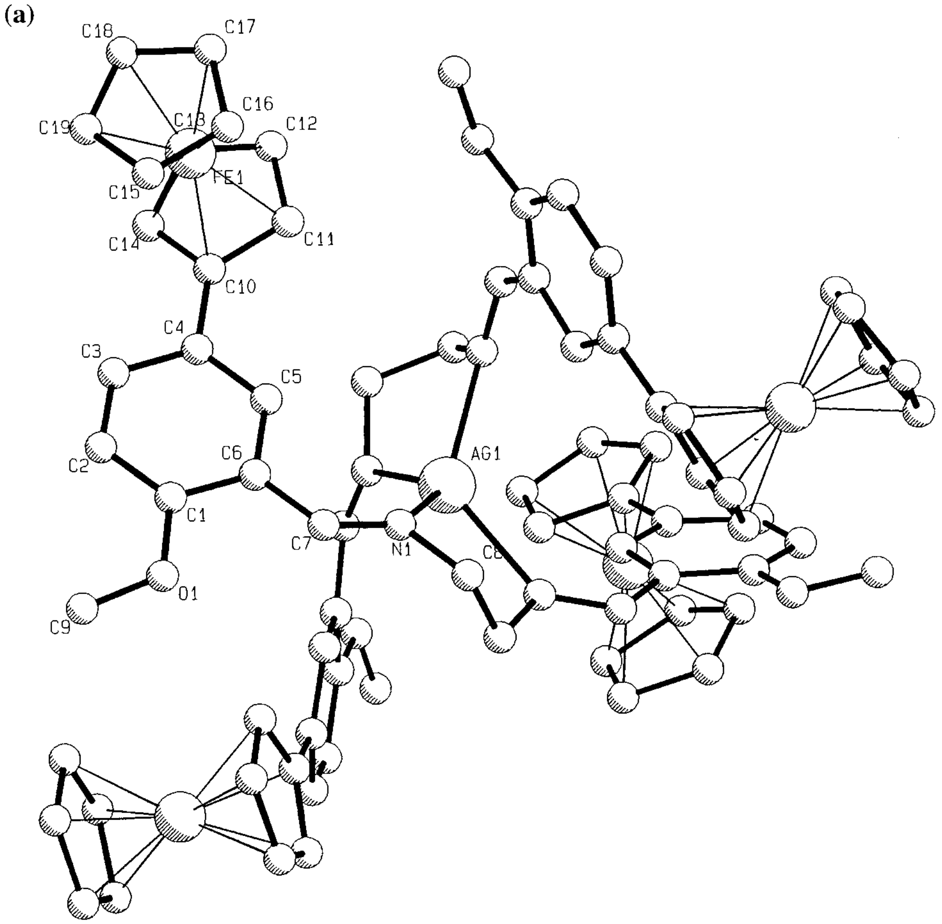


Fig. 3. The X-ray crystal structure of the complex of **9** with Ag^+: (a) showing the tetrahedral arrangement around Ag^+ and (b) showing the α-helical array of two ligand molecules around Ag^+.

3.2. Complexation of 9

Bis(3-ethylenediimino-4-methoxyphenyl)ferrocene, **9**, was treated with a 1:1 molar equivalent each of $Cu(MeCN)_4BF_4$, $Zn(CF_3SO_3)_2$, $NiCl_2 \cdot D_2O$ and $AgBF_4$ in acetonitrile (or CD_3CN). With zinc triflate in CD_3CN a slow decomposition of the imine to aldehyde was observed by NMR, presumably due to adventitious water. The complex with $NiCl_2 \cdot 6D_2O$ in $CD_3CN/CDCl_3$ was also unstable, so the only reliable results were obtained with Cu^+ and Ag^+.

3.2.1. Complexation with Cu(I) and Ag(I) by NMR

A 1:1 complex of **9** with $Cu(MeCN)_4BF_4$ was precipitated from acetonitrile by addition of diethylether. The complex was characterised by elemental analysis and MS (see Section 2) and Fig. 1 shows the ^1H-NMR spectrum of the complex in $CDCl_3/CD_3CN$ relative to the ligand. Significant upfield shifts (0.4 ppm) were found for the bridging N-methylene protons on complexation. The imine proton broadened and the single aromatic proton adjacent to the imino function both broadened and shifted downfield by 0.17 ppm, implying an intensification of the aromatic diamagnetic anisotropy. The doublets assigned to the remaining aromatic protons also broadened slightly and shifted to lower field in the complex and overall, the data suggest a dynamic phenomenon associated with the complex with a rate that is close to the NMR time scale. The cyclopentadiene protons remained virtually unaffected and the methoxy protons shifted slightly downfield by 0.15 ppm (Table 1). The NMR spectra for the complex of **9** with Ag^+ showed different behaviour. Only the bridging N-methylene protons broadened compared with the free ligand and no broadening was observed in the aromatic region. The doublet at 8.00 ppm in the ligand moved upfield by 0.2 ppm in the complex, whereas the doublet and doublet of doublets at 6.79 and 7.47 ppm, respectively, both moved downfield slightly with all the signals remaining sharp. The imino proton moved upfield slightly (0.11 ppm) and also remained sharp but all the remaining protons were almost unaffected. The ^{13}C spectrum of the ligand is very similar to that of its two complexes (Table 2) except that in both cases the imino carbon moved downfield on complexation by 4.9 ppm for Ag^+ and by

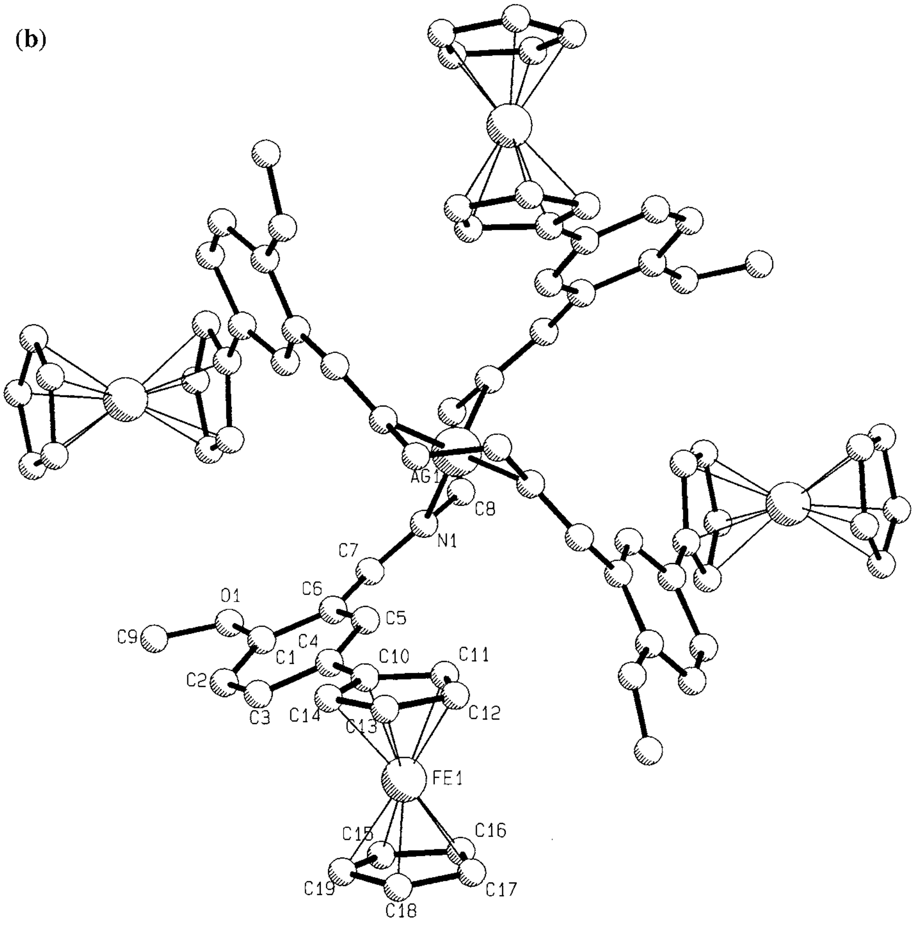


Fig. 3. (*Continued*)

1.9 ppm for Cu^+. Thus, the NMR data suggest that two different types of complex are formed with Ag^+ and Cu^+ but offer very little evidence to elucidate the structures.

3.2.2. Complexation by cyclic voltammetry and UV/vis spectrometry

A cyclic voltammogram of the complex of **9** with $CuBF_4$ in CH_2Cl_2 gave a redox potential of 410 mV compared with 450 mV (reference Ag/AgCl in 3 M NaCl) for the free ligand (Fig. 2). The cathodic shift of 40 mV indicates a slight increase in electron density at the ferrocene centres making it easier to oxidise the metal. The observation of only one redox wave for both iron centres in ligand or complex however, indicates no interaction between the ferrocene units. The intensity of the UV absorption due to the d–d transition of ferrocene at 450 nm in the Cu(I) complex ($\varepsilon = 17760$ $l\,mol^{-1}\,cm^{-1}$) was almost twice as high as that in the free ligand ($\varepsilon = 8000$ $l\,mol^{-1}\,cm^{-1}$) but no significant shift in λ_{max} was observed. Thus, the energy of the UV transition remained unaffected but the polarity change during the transition was clearly enhanced. No satisfactory CV data was recorded with the Ag(I) complex due to deposition of the complex (or Ag) on the surface of the working electrode. Furthermore, no definite UV data was obtained for the Ag^+ complex.

3.2.3. By X-ray crystallography

Slow evaporation of the NMR solution of the Ag^+ complex gave single crystals suitable for X-ray crystallography. The crystal belonged to the cubic system (F4 3d), a highly unusual feature for organometallic complexes. Even more remarkable was the finding that the complex involved a distorted tetrahedral configuration of the four imino nitrogens of the two ligand molecules around the central Ag^+ ion in a helical arrangement that had spontaneously resolved (Fig. 3(a) and (b)). A selection of bond lengths and bond angles is given in Table 3, from which it is clear that the Ag–N distance is 2.334(3) Å throughout but the N–Ag–N bond angles are either 76.3(3)° or 128.2(2)°. The ferrocene units and the aromatic rings are then situated in an α-helical array around Ag^+ and the methoxy groups play no part in the coordination sphere. This is at least consistent with the NMR data since the imino carbon of the complex moves downfield by 4.9 ppm and the methoxy protons and carbons are only slightly perturbed.

Table 3
Bond lengths (Å) and angles (°) for Schiff base–Ag^+ complex

Bond lengths (Å)	
Ag(1)–N(1)	2.344 (6)
N(1)–C(7)	1.275 (10)
N(1)–C(8)	1.500 (10)
(2)C(4)–C(10)	1.450 (11)
Bond angles (°)	
$N(1)^{\#1}$–Ag(1)–$N(1)^{\#2}$	76.3 (3)
$N(1)^{\#1}$–Ag(1)–N(1)	128.2 (2)
C(1)–O(1)–C(9)	116.8 (8)
C(7)–N(1)–C(8)	118.6 (7)
C(7)–N(1)–Ag(1)	132.3 (6)
C(8)–N(1)–Ag(1)	107.1 (5)
O(1)–C(1)–C(6)	116.2 (7)
O(1)–C(1)–C(2)	123.6 (8)
C(6)–C(1)–C(2)	120.2 (8)
C(3)–C(4)–C(10)	121.4 (8)
C(5)–C(4)–C(10)	120.8 (7)
C(4)–C(5)–C(6)	122.0 (7)
C(1)–C(6)–C(7)	120.0 (7)
C(5)–C(6)–C(7)	121.7 (8)
N(1)–C(7)–C(6)	125.3 (7)
$C(8)^{\#3}$–C(8)–N(1)	108.9 (7)
C(14)–C(10)–C(4)	126.7 (8)
C(11)–C(10)–C(4)	126.8 (8)

3.3. Complexation of 12

Since only a small quantity of the ligand was available, the complexes were not isolated but their formation was monitored by ^1H- and ^{13}C-NMR (Table 4) with a 1:1 molar ratio of ligand:cation in solution. Complexation with Cu(I) showed similar changes to those observed for the complexation of **9** with Cu(I). The signals assigned to the cyclopentadiene protons became broad and moved closer together and all the protons of the aromatic rings moved to lower field by ca. 0.5 ppm. In contrast to the complex of Cu(I) with **9** however, the CH=N proton moved downfield by ca. 0.15 ppm. The central methylene protons were obscured by solvent peaks but the N-methylene protons at 4.19 ppm and the shifts of the aromatic protons suggest coordination of the Cu^+ ion by the imine nitrogens inside the macrocycle. The ^{13}C-NMR seems to confirm this conclusion since the imino carbon moves downfield by 4.7 ppm and the remaining carbons also show slight downfield shifts.

With Ag^+, the ^1H-NMR spectra were very broad and no reliable assignments could be made. The ^{13}C-NMR however, again showed a series of downfield shifts with the most pronounced being that of the imino carbon with a $\Delta\delta$ value of 5.3 ppm. It seems likely therefore, that the Ag^+ ion is also encapsulated within the macrocycle by coordination to the imino functions. A cyclic voltammogram was recorded for the free ligand only and gave a redox potential of 0.42 V in CH_2Cl_2, which is slightly more positive than the redox potential of ligand **9**.

4. Conclusion

Two types of Schiff base hosts (**9** and **12**) containing ferrocene have been prepared and characterised. Both form complexes with Ag^+ and Cu^+ as detected by NMR and/or UV/vis spectroscopy together with cyclic voltammetry. The complex of **9** with Ag^+ gives a well-defined tertrahedral configuration of two molecules of the ligand to each Ag^+ ion, which resolves spontaneously into an α-helical array in the crystal.

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Table 4
The ^1H- and ^{13}C-NMR spectra of ligand 12 and its complex with $CuBF_4$ and $AgBF_4$

	OCH_3	CH_2	$H_{\alpha,\beta}$	H_{Φ}	CH=N
δ (ppm)	3.79 (s)	2.30 (m), 3.88 (m)	4.27 (t, $J=1.8$Hz), 4.56 (t, $J=1.8$Hz)	6.53 (d, $J=8.6$Hz), 7.00 (dd, $J=8.6$Hz), 7.65 (d, $J=2.4$Hz)	8.55 (s)
$CuBF_4$ δ (ppm)	3.91 (s)	—, 4.19 (br)	4.34 (br), 4.39 (br)	6.92 (d, $J=8.6$Hz), 7.52 (d, $J=8.0$Hz), 8.13 (s)	8.72 (s)
	OCH_3	CH_2	$C_{\alpha,\beta}$	C_{ϕ}	C_{imino}
δ (ppm)	54.9	28.4, 63.0	65.4, 68.0	110.4 (CH), 123.4 (CH), 127.9 (CH)	156.9
$CuBF_4$ δ (ppm)	56.2	29.8, 32.4, 64.2	68.0, 70.0	112.1 (CH), 123.5 (CH), 131.4 (CH)	161.6
$AgBF_4$ δ (ppm)[a]	55.6	29.7, 31.9, 63.9	67.6	109.4 (CH), 125.3 (CH), 132.9 (CH)	162.2

[a] In $CD_3CN:CDCl_3$ (2:1).

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