New Bis(Ferrocenecarbonyl)- and Bis(ferrocenyl)-appended Diazatetrathia Mixed-donor Macrocyclic Ligands and their Copper-(II) and -(I) Complexes‡

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New bis(ferrocenecarbonyl)-, bis(ferrocenyl)- and dibenzyl-appended diazatetrathia mixed-donor macrocyclic ligands L^1, L^2 and L^3 have been prepared. Copper-(II) and -(I) complexes of these ligands have been isolated and characterised. Single-crystal X-ray structures of 7,16-bis(ferrocenemethyl)-1,4,10,13-tetrathia-7,16-diazacyclooctadecane (L^2) and of its copper(I) complex $[CuL^2]PF_6$ have also been determined. Electrochemical investigations reveal the respective ferrocene–ferrocenium redox couples of ligands L^1 and L^2 are perturbed to more positive potentials on co-ordination of the copper(II) ion. These copper(II) complexes also exhibit quasi-reversible copper(II)–copper(I) redox couples at negative potentials (*versus* saturated calomel electrode).

Heteropolymetallic assemblies consisting of organometallic redox-active moieties covalently attached to macrocyclic complexes of co-ordinatively unsaturated transition metals provide exciting future prospects for small-molecule activation at multinuclear metal sites.[1–3] Fig. 1 depicts the essential features of one such system. Activation of small molecules such as carbon monoxide, olefins, *etc.* bound to the co-ordinated transition-metal centre may produce new synthetic pathways to coupled redox reaction products in a stoichiometric or catalytic fashion. Towards this objective and as part of a research programme aimed at incorporating metallocene redox-active centres into various macropolycyclic host structural environments,[4] we report here the syntheses, co-ordination and electrochemical studies of bis(ferrocenylcarbonyl) and bis(ferrocenyl) appended diazatetrathia mixed-donor macrocycles, including the X-ray structural studies of one ligand and of its copper(I) complex.

Experimental

Solvent and Reagent Pretreatment.—Where necessary solvents were purified by distillation prior to use. Acetonitrile was distilled from CaH_2, dichloromethane from P_2O_5, hexane and diethyl ether from sodium, toluene and tetrahydrofuran (thf) from sodium using benzophenone as the indicator, dimethylformamide (dmf) under reduced pressure from $MgSO_4$ and thionyl chloride from triphenyl phosphite.

Unless otherwise stated, commercial grade chemicals were used without further purification. 1,4,10,13-tetrathia-7,16-diazacyclooctadecane **1**,[5] ferrocenylcarbonyl chloride **2**[6] and (ferrocenylmethyl)trimethylammonium iodide **3**[7] were prepared according to the literature procedures.

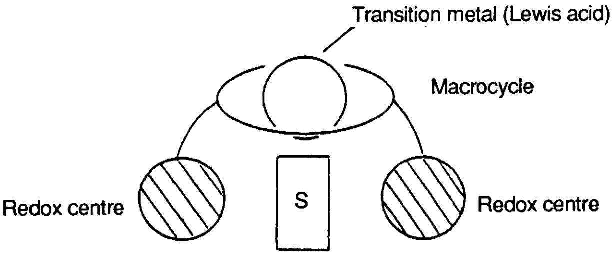

Fig. 1 The principle of catalytic polymetallic activation of an included substrate S by a redox-active macrocyclic system

Instrumental Methods.—Melting points were recorded on a Gallenkamp apparatus in open capillaries and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 297 instrument (4000–600 cm^{-1}) as KBr discs, nuclear magnetic resonance spectra on JEOL FX-90Q, GX-270 and Bruker WH400 instruments using tetramethylsilane as internal standard. Mass spectra and fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS80 RF mass spectrometer, using an argon primary beam and 3-nitrobenzyl alcohol as the matrix. The ultraviolet–visible spectra were recorded on a Shimadzu uv-240 spectrophotometer. All elemental analyses were performed at the University of Birmingham.

Electrochemical Measurements.—Cyclic voltammetry, differential pulse voltammetry and controlled-potential electrolysis were carried out with a PAR 174A potentiostat. All the electrochemical measurements were performed under nitrogen, and used $[NBu^n_4][BF_4]$ as the supporting electrolyte.

The cyclic voltammetry and differential pulse voltammetry measurements were carried out using a three-electrode cell, which incorporated a saturated calomel reference electrode (SCE), a platinum-wire auxiliary electrode and a platinum-bead working electrode. The current *vs.* voltage curves were recorded with a Philips X-Y recorder.

During the controlled-potential electrolysis a large platinum-gauze electrode was placed in the main cell compartment

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containing the stirred test solution. The counter electrode was another large platinum-gauze square, held in a secondary cell compartment isolated by a sintered-glass disc. The current passed was measured using a Hi-tek electronic integrator, which was calibrated in conjunction with the cell using a known amount of ferrocene.

Syntheses.—7,16-*Bis(ferrocenylcarbonyl)*-1,4,10,13-*tetrathia*-7,16-*diazacyclooctadecane* (L^1). Ferrocenylcarbonyl chloride **2** (0.36 g, 1.2 mmol) was dissolved in dry dichloromethane (50 cm^3) and added dropwise to a stirred solution of 1,4,10,13-tetrathia-7,16-diazacyclooctadecane **1** (0.13 g, 0.39 mmol) and triethylamine (0.13 g, 1.3 mmol) in dry dichloromethane (50 cm^3). The solution was warmed to reflux and heating continued for 12 h. After cooling, the solution was washed with distilled water (50 cm^3) to remove triethylamine hydrochloride. The organic layer was retained and the product purified by column chromatography [alumina, dichloromethane–methanol (97:3 v/v) as eluent]. The product was an orange oily solid, which when washed with hexane became an orange powder L^1, yield 0.19 g (64%), m.p. 183–184 °C. IR/cm^{-1} (KBr): 3095 (C–H str of ferrocene), 2900, 2800 (alkyl C–H) and 1640 (C=O str). ^1H NMR ($CDCl_3$): δ 4.50 (8 H, s, H of substituted C_5H_4), 4.25 (10 H, s, H of unsubstituted C_5H_5), 3.80 (8 H, m, NCH_2CH_2S) and 2.9 (16 H, m, NCH_2CH_2S and SCH_2CH_2S). Electron impact (EI) mass spectrum: *m*/*z* 750 (M^+) (Found: C, 54.2; H, 6.0;, N, 3.4. Calc. for $C_{34}H_{42}Fe_2N_2O_2S_4$: C, 54.4; H, 5.6; N, 3.7%).

7,16-*Bis(ferrocenylmethyl)*-1,4,10,13-*tetrathia*-7,16-*diazacyclooctadecane* (L^2). Compound **1** (0.10 g, 0.3 mmol) was dissolved in dry acetonitrile (100 cm^3) with anhydrous potassium carbonate (0.77 g, 2 mmol). To this was added (ferrocenylmethyl)trimethylammonium iodide **3** (0.24 g, 6.2 mmol) and the solution heated to reflux for 24 h. During this time trimethylamine evolved which was detected by pink litmus paper. After cooling, potassium carbonate was filtered off, the acetonitrile removed and the yellow solid residue taken up in dichloromethane. The solution was washed with distilled water (3 × 50 cm^3) to remove unreacted ferrocene quaternary ammonium salt and the organic layer retained. The product was purified by column chromatography on alumina [dichloromethane–methanol (99:1 v/v) as eluent] and a pale yellow powder L^2 was produced, yield 0.10 g (45%), m.p. 173–174 °C. IR/cm^{-1} (KBr): 3090 (C–H str. of ferrocene), 2950, 2800 (alkyl C–H str.). ^1H NMR ($CDCl_3$): δ 4.1 (18 H, s, H of ferrocene), 3.50 (4 H, s, $C_5H_4CH_2N$), 2.72 (8 H, s, NCH_2CH_2S) and 2.60 (16 H, s, NCH_2CH_2S and SCH_2CH_2S). EI mass spectrum: *m*/*z* 722 (M^+) (Found: C, 56.3; H, 6.1; N, 4.0. Calc. for $C_{34}H_{46}Fe_2N_2S_4$: C, 56.5; H, 6.4; N, 3.9%).

7,16-*Dibenzyl*-1,4,10,13-*tetrathia*-7,16-*diazacyclooctadecane* L^3. Benzyl bromide (0.63 g, 4 mmol) was dissolved in dry acetonitrile (40 cm^3) and added dropwise to a refluxing solution of compound **1** (0.30 g, 0.9 mmol) and anhydrous potassium carbonate (1.27 g, 0.9 mmol) in acetonitrile (40 cm^3). The mixture was heated to reflux for 96 h. After cooling, it was filtered to remove potassium carbonate and potassium bromide and the product purified by column chromatography on alumina. The first band (dichloromethane eluent) was benzyl bromide. The second band yielded compound L^3 [dichloromethane–methanol (98:2 v/v) as eluent], a colourless oil, yield 0.44 g (95%). IR/cm^{-1} (KBr): 3050 (aromatic C–H str), 2900, 2800 (alkyl C–H str). ^1H NMR ($CDCl_3$): δ 7.32 (10 H, s, aromatic H), 3.67 (4 H, m, $PhCH_2N$) and 2.88 (24 H, br m, NCH_2CH_2S and SCH_2CH_2S). EI mass spectrum: *m*/*z* 507 (M^+) (Found: C, 62.0; H, 7.9; N, 5.6. Calc. for $C_{26}H_{38}N_2S_4$: C, 61.5; H, 7.5; N, 5.5%).

Table 1 Fractional atomic coordinates (× 10^4) for ligand L^2

Atom	*x*	*y*	*z*
Fe(1)	8 790(1)	10 067(1)	6 597(1)
N(1)	6 882(3)	7 330(6)	5 966(6)
C(2)	6 230(5)	7 449(10)	6 760(11)
C(3)	5 863(5)	8 841(12)	6 269(12)
S(4)	5 072(1)	8 972(3)	7 110(2)
C(5)	4 519(4)	7 819(10)	5 905(8)
C(6)	3 794(4)	8 018(9)	6 167(8)
S(7)	3 163(1)	7 181(2)	4 869(2)
C(8)	3 369(5)	5 216(10)	5 036(10)
C(9)	2 906(5)	4 266(10)	4 012(9)
C(10)	8 037(3)	8 527(7)	5 973(6)
C(11)	8 685(3)	7 774(7)	6 282(7)
C(12)	9 150(4)	8 401(8)	5 424(7)
C(13)	8 788(4)	9 504(8)	4 570(7)
C(14)	8 119(4)	9 588(7)	4 898(7)
C(15)	9 041(8)	10 470(11)	8 634(8)
C(16)	9 583(6)	10 870(15)	7 903(15)
C(17)	9 361(6)	11 966(12)	7 031(11)
C(18)	8 704(6)	12 279(10)	7 095(10)
C(19)	8 482(6)	11 394(15)	8 119(13)
C(0)	7 422(4)	8 313(9)	6 714(8)

Table 2 Selected bond lengths (Å) and angles (°) for ligand L^2

C(0)–N(1)	1.482(10)	C(19)–C(18)	1.372(18)
C(3)–C(2)	1.465(15)	N(1)–C(9′)	1.461(10)
C(5)–S(4)	1.803(10)	N(1)–C(2)	1.571(14)
S(7)–C(6)	1.809(10)	S(4)–C(3)	1.838(13)
C(9)–C(8)	1.510(14)	C(6)–C(5)	1.480(12)
C(14)–C(10)	1.420(10)	C(8)–S(7)	1.771(11)
C(12)–C(11)	1.417(11)	C(11)–C(10)	1.427(10)
C(14)–C(13)	1.386(12)	C(0)–C(10)	1.487(11)
C(16)–C(15)	1.390(20)	C(13)–C(12)	1.407(11)
C(17)–C(16)	1.318(18)	C(19)–C(15)	1.402(19)
C(18)–C(17)	1.322(18)		
C(0)–N(1)–C(2)	107.0(7)	C(0)–N(1)–C(9′)	106.39(10)
S(4)–C(3)–C(2)	108.2(9)	C(3)–C(2)–N(1)	106.9(9)
C(6)–C(5)–S(4)	109.6(7)	C(5)–S(4)–C(3)	98.5(5)
C(8)–S(7)–C(6)	101.6(5)	S(7)–C(6)–C(5)	114.8(7)
C(14)–C(10)–C(11)	106.4(7)	C(9)–C(8)–S(7)	111.3(7)
C(0)–C(10)–C(14)	127.4(7)	C(0)–C(10)–C(11)	126.1(7)
C(13)–C(12)–C(11)	107.4(7)	C(12)–C(11)–C(10)	108.3(7)
C(13)–C(14)–C(10)	109.1(7)	C(14)–C(13)–C(12)	108.8(7)
C(17)–C(16)–C(15)	107.3(12)	C(19)–C(15)–C(16)	106.4(10)
C(19)–C(18)–C(17)	108.1(11)	C(18)–C(17)–C(16)	111.6(12)
C(18)–C(19)–C(15)	106.5(12)	C(10)–C(0)–N(1)	113.9(7)
C(2)–N(1)–C(9′)	106.38(12)	N(1)–C(9′)–C(8′)	109.02(7)

(7,16-*Dibenzyl*-1,4,10,13-*tetrathia*-7,16-*diazacyclooctadecane copper*(II) *tetrafluoroborate dihydrate* $[CuL^3][BF_4]_2 \cdot 2H_2O$. Ligand L^3 (0.10 g, 0.2 mmol) was dissolved in absolute ethanol (50 cm^3). To this was added copper(II) tetrafluoroborate hexahydrate (0.07 g, 0.2 mmol) with stirring. Instantly a colour change was observed from colourless to pale green. The solution was allowed to stir at room temperature for 24 h. The ethanol was then removed to yield a green solid which was recrystallised from hot ethanol, yield 0.20 g (31%), m.p. 180 °C (decomp.). IR/cm^{-1} (KBR) 3090 and 2900 (aromatic C–H and alkyl C–H str), 1040 (BF_4^- str). FAB mass spectrum: *m*/*z* 659 $(M - BF_4)^+$ (Found: C, 39.6; H, 5.0; N, 3.4. Calc. for $C_{26}H_{42}B_2CuF_8N_2O_2S_4$: C, 40.0; H, 5.4; N, 3.6%).

[7,16-*Bis(ferrocenylcarbonyl)*-1,4,10,13-*tetrathia*-7,16-*diazacyclooctadecane*]*copper*(II) *tetrafluoroborate* $[CuL^1][BF_4]_2$. The same procedure as above was used with L^1. An apple-green powder was produced, yield 0.05 g (37%), m.p. 192 °C (decomp.). IR/cm^{-1} (KBr): 3100, 2900 (ferrocene and alkyl C–H str), 1640 (C=O str) and 1040 (BF_4^-). FAB mass spectrum: *m*/*z* 814 $(M - BF_4)^+$ (Found: C, 40.2; H, 4.5; N, 2.5. Calc. for $C_{34}H_{42}B_2CuF_8Fe_2N_2O_2S_4$: C, 39.8; H, 4.5; N, 2.7%).

[7,16-*Bis(ferrocenylmethyl)*-1,4,10,13-*tetrathia*-7,16-*diazacyclooctadecane*]*copper*(II) *tetrafluoroborate dihydrate* $[CuL^2][BF_4]_2 \cdot 2H_2O$. The same synthetic procedure was employed as for ligand L^3 but using ligand L^2. A dark green powder was produced which was recrystallised from acetonitrile and ethanol, yield 0.06 g (45%), m.p. 180 °C (decomp.). IR/cm^{-1}

Table 3 Fractional atomic coordinates for $[CuL^2]PF_4$ in the atom numbering, read 2,3 (in place of 1) for the first digit as appropriate for 'molecules' 2 and 3

	'Molecule' 1			'Molecule' 2			'Molecule' 3		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.921 91(9)	0.070 6(1)	0.832 4(1)	0.443 78(9)	0.023 8(1)	0.740 07(9)	0.252 36(9)	0.454 7(1)	1.109 1(1)
Fe(1)	0.618 5(1)	0.242 6(1)	0.843 8(1)	0.732 0(1)	0.012 7(1)	0.567 5(1)	−0.054 1(1)	0.632 1(1)	1.121 2(1)
Fe(1′)	0.889 2(1)	0.359 6(1)	0.501 0(1)	0.385 7(1)	0.350 0(1)	0.438 3(1)	0.376 1(2)	0.562 5(2)	0.629 4(2)
N(11)	0.784 7(6)	0.130 5(6)	0.989 6(6)	0.587 8(5)	−0.114 6(6)	0.679 2(6)	0.110 6(5)	0.529 8(6)	1.250 7(6)
C(12)	0.800 6(7)	0.191 4(8)	0.982 4(8)	0.567 4(7)	−0.118 4(7)	0.615 5(8)	0.130 6(7)	0.590 9(8)	1.248 4(8)
C(13)	0.877 0(7)	0.182 2(8)	0.948 5(8)	0.488 2(7)	−0.085 9(8)	0.624 1(8)	0.208 1(7)	0.578 3(8)	1.210 9(8)
S(14)	0.899 5(2)	0.189 1(2)	0.840 6(2)	0.448 6(2)	0.017 4(2)	0.618 5(2)	0.228 1(2)	0.579 7(2)	1.106 0(2)
C(15)	0.990 8(7)	0.185 0(8)	0.810 6(8)	0.355 8(7)	0.038 3(8)	0.629 5(9)	0.317 5(8)	0.580 1(8)	1.069 0(9)
C(16)	1.045 8(7)	0.102 6(9)	0.837 3(8)	0.316 4(7)	0.009 6(8)	0.718 3(9)	0.374 0(7)	0.498 4(9)	1.101 0(8)
S(17)	1.046 6(2)	0.032 2(2)	0.803 4(2)	0.321 0(2)	0.048 7(2)	0.786 7(2)	0.375 4(2)	0.420 3(2)	1.079 0(3)
C(18)	1.085 4(7)	0.067 1(9)	0.692 8(9)	0.263 4(7)	0.153 2(8)	0.748 3(8)	0.414(1)	0.454(2)	0.964(1)
C(19)	1.063 7(9)	0.046 8(9)	0.640 6(9)	0.282 6(7)	0.204 9(8)	0.766 3(8)	0.402(1)	0.421(1)	0.921(1)
N(11′)	0.992 0(6)	0.098 9(7)	0.628 9(7)	0.345 3(5)	0.221 9(6)	0.708 4(6)	0.332 9(8)	0.455 5(9)	0.901 2(9)
C(12′)	0.957 3(8)	0.061 7(9)	0.614 1(8)	0.384 5(7)	0.239 0(8)	0.742 7(8)	0.306(1)	0.398(1)	0.909(1)
C(13′)	0.931 2(8)	0.002 4(8)	0.692 1(9)	0.427 1(7)	0.164 1(8)	0.801 8(7)	0.267 3(9)	0.367(1)	0.984(1)
S(14′)	0.865 0(2)	0.058 6(2)	0.760 6(2)	0.494 8(2)	0.095 0(2)	0.749 0(2)	0.200 8(2)	0.435 8(2)	1.036 8(2)
C(15′)	0.835 1(8)	−0.022(1)	0.840 5(9)	0.541 6(7)	0.018 2(8)	0.831 2(9)	0.160 8(8)	0.368(1)	1.122(1)
C(16′)	0.887 0(9)	−0.083 9(9)	0.896 9(9)	0.502 1(8)	−0.039 1(9)	0.896 7(8)	0.206 0(9)	0.307 7(9)	1.186 4(9)
S(17′)	0.906 8(2)	−0.041 4(2)	0.949 5(2)	0.481 6(2)	−0.087 9(2)	0.856 8(2)	0.228 6(2)	0.352 1(2)	1.230 6(2)
C(18′)	0.823 4(7)	−0.015 7(8)	1.023 8(8)	0.568 7(7)	−0.162 3(7)	0.832 9(8)	0.144 2(7)	0.382 9(7)	1.312 3(8)
C(19′)	0.809 5(7)	0.052 7(8)	1.044 5(8)	0.577 6(7)	−0.179 5(8)	0.757 7(9)	0.134 4(7)	0.455 5(8)	1.317 2(8)
C(10)	0.708 6(7)	0.155 0(8)	0.985 1(8)	0.661 2(8)	−0.119 2(9)	0.655(1)	0.031 9(7)	0.558 2(8)	1.264 0(8)
C(110)	0.680 9(8)	0.227 6(8)	0.912 6(9)	0.673 8(8)	−0.047 5(9)	0.580 9(9)	0.001 9(8)	0.628 6(8)	1.190 4(8)
C(111)	0.615 6(7)	0.292 9(9)	0.918 3(9)	0.731 3(7)	−0.052(1)	0.510(1)	0.036 0(7)	0.646 8(8)	1.106 7(9)
C(112)	0.609 7(8)	0.351 1(8)	0.838(1)	0.722 3(9)	0.026(1)	0.456 4(9)	−0.010 1(8)	0.716 7(9)	1.058 9(8)
C(113)	0.672 6(9)	0.318(1)	0.782 1(8)	0.660 6(9)	0.079 0(9)	0.492(1)	−0.074 9(8)	0.743 9(8)	1.116(1)
C(114)	0.715 0(7)	0.245 4(9)	0.828(1)	0.631 0(8)	0.033(1)	0.568(1)	−0.065 4(8)	0.688 3(9)	1.194 0(9)
C(115)	0.636(1)	0.156(1)	0.807(2)	0.757(2)	0.089(2)	0.583(2)	−0.031(1)	0.545(1)	1.078(1)
C(116)	0.600(1)	0.140(1)	0.890(1)	0.728(2)	0.040(3)	0.660(2)	−0.060(1)	0.524(1)	1.162(1)
C(117)	0.537(1)	0.205(1)	0.891(1)	0.771(2)	−0.037(3)	0.672(1)	−0.127(1)	0.579(1)	1.174(1)
C(118)	0.532(1)	0.261(1)	0.811(1)	0.826(1)	−0.038(2)	0.601(3)	−0.138(1)	0.636(1)	1.097(2)
C(119)	0.595(1)	0.229(1)	0.758(1)	0.816(2)	0.039(3)	0.551(2)	−0.080(2)	0.617(2)	1.036(1)
C(10′)	0.989 6(8)	0.177(1)	0.561 3(8)	0.325 1(7)	0.287 7(8)	0.631 9(8)	0.326 9(9)	0.521 7(9)	0.825(1)
C(110′)	0.918 1(8)	0.241 6(9)	0.574 0(9)	0.388 1(7)	0.288 3(8)	0.560 7(8)	0.380(1)	0.500(1)	0.750(1)
C(111′)	0.900 2(9)	0.290(1)	0.619 9(9)	0.427(1)	0.340 1(9)	0.525(1)	0.384(1)	0.452(1)	0.713(1)
C(112′)	0.829 5(9)	0.343(1)	0.618 5(9)	0.481(1)	0.316(1)	0.461(1)	0.444(2)	0.446(1)	0.647(2)
C(113′)	0.802 1(8)	0.330(1)	0.573 3(9)	0.478 2(9)	0.252(1)	0.454(1)	0.478(1)	0.490(1)	0.643(1)
C(114′)	0.858(1)	0.265(1)	0.544 0(9)	0.420 8(8)	0.235 0(8)	0.516 1(9)	0.440 4(9)	0.524 6(9)	0.707(1)
C(115′)	0.967(1)	0.404(2)	0.447(2)	0.318(2)	0.360(1)	0.381(2)	0.283(1)	0.751(1)	0.624(1)
C(116′)	0.902(2)	0.467(1)	0.454(1)	0.285 1(9)	0.411(2)	0.423(1)	0.332(1)	0.687(1)	0.589(2)
C(117′)	0.860(1)	0.468(1)	0.412(2)	0.316(2)	0.464(1)	0.397(2)	0.371(1)	0.661(1)	0.524(1)
C(118′)	0.900(2)	0.411(2)	3.771(1)	0.374(1)	0.445(2)	0.333(2)	0.349(1)	0.607(1)	0.520(2)
C(119′)	0.968(2)	0.368(1)	0.399(2)	0.373(1)	0.381(2)	0.324(1)	0.292(1)	0.601(1)	0.588(2)
P(1)	0.297 1(2)	0.136 3(3)	1.038 3(3)	0.147 6(2)	0.265 7(3)	0.569 7(3)	0.401 4(3)	−0.283 2(4)	0.816 0(3)
F(11)	0.295 5(5)	0.063 3(5)	1.121 0(5)	0.166 3(5)	0.300 2(5)	0.615 7(5)	0.339 0(7)	−0.308(1)	0.859(1)
F(12)	0.217 5(4)	0.186 2(5)	1.069 9(5)	0.132 7(6)	0.346 5(6)	0.500 6(6)	0.444(1)	−0.367 0(9)	0.812(1)
F(13)	0.377 6(4)	0.086 2(5)	1.006 0(5)	0.069 5(5)	0.287 6(7)	0.616 3(6)	0.383(1)	−0.254(2)	0.737(1)
F(14)	0.298 9(5)	0.209 4(5)	0.954 3(5)	0.129 0(5)	0.230 0(6)	0.524 3(6)	0.466 7(8)	−0.264(1)	0.771(1)
F(15)	0.323 3(5)	0.170 3(6)	1.076 8(6)	0.164 9(7)	0.181 8(6)	0.639 8(7)	0.358(1)	−0.202 1(9)	0.817(1)
F(16)	0.272 0(5)	0.102 5(6)	0.997 4(5)	0.227 5(5)	0.236 1(7)	0.530 1(8)	0.418(1)	−0.317(1)	0.897 3(9)
Dichloromethane									
C[a]	0.044(4)	−0.245(3)	0.708(4)	Cl(2)[a]	−0.035(7)	−0.23(1)	0.757(4)		
Cl(1)[a]	0.056(9)	−0.17(1)	0.629(2)						
Hexane									
C(1)	0.180(1)	−0.177(1)	0.710 3(9)	C(5)	0.132 9(8)	−0.329 1(8)	0.867 7(9)		
C(2)	0.176(1)	−0.171(1)	0.786(1)	C(6)[b]	0.096 2(8)	−0.262(1)	0.795(1)		
C(3)	0.122 0(9)	−0.204 2(9)	0.854 4(9)	C(7)[b]	0.099(1)	−0.373(1)	0.854(1)		
C(4)	0.165 1(9)	−0.289 5(9)	0.880 4(8)						

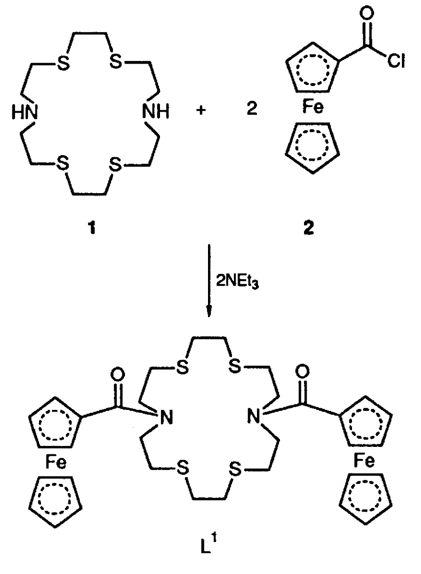
[a] Site occupancy 0.744(9). [b] Site occupancy 0.5.

(KBr): 3025, 2900 (ferrocene and alkyl C–H str), 1020 (BF_4^-). FAB mass spectrum: *m/z* 960 (M^+) and 872 ($M - BF_4$) (Found: C, 41.3; H, 4.6; N, 2.9. Calc. for $C_{34}H_{50}B_2CuF_8N_2O_2S_4$: C, 41.0; H, 5.0; N, 2.8%).

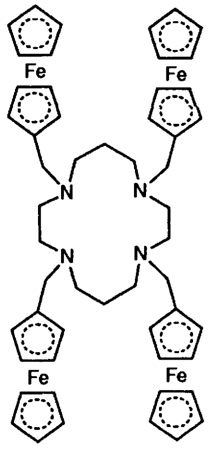
[7,16-*Bis(ferrocenylmethyl)*-1,4,10,13-*tetrathia*-7,16-*diazacyclooctadecane*]*copper*(I) *hexafluorophosphate* $[CuL^2]PF_6$. Ligand L^2 (0.044 g, 0.061 mmol) was dissolved in acetonitrile–dichloromethane (80:20 v/v) under nitrogen. To the solution was added tetrakis(acetonitrile) copper(I) hexafluorophosphate in acetonitrile (0.023 g, 0.061 mmol in 5 cm^3) using Schlenk-line techniques. On addition of the copper(I) salt the ligand, which had been sparingly soluble, gradually dissolved to give a clear yellow solution. This was stirred under nitrogen for 1 h, after which time the solvent was removed to give an orange solid which was recrystallised from dichloromethane and acetonitrile, yield 0.025 g (44%), m.p. 210 °C (decomp.). IR/cm^{-1} (KBr): 3075, 2910 (ferrocene and alkyl C–H str), 835 (PF_6^-). ^{1}H NMR ($CDCl_3$): δ 4.15 (18 H, H of ferrocene), 3.48 (4 H, m, $C_5H_4CH_2N$) and 3.65 (24 H, m, SCH_2CH_2S and NCH_2CH_2S). FAB mass spectrum: *m*/*z* 785 ($[CuL]^+$) (Found: C, 44.5; H, 5.1; N, 3.4. Calc. for $C_{34}H_{46}CuF_6Fe_2N_2PS_4$: C, 43.8; H, 4.9; N, 3.5%).

Structure Determinations.—Compound L^2. *Crystal data.* $C_{34}H_{46}Fe_2N_2S_4$, *M* = 724.72, monoclinic, space group $P2_1/c$ *a* = 19.554(3), *b* = 8.760(1), *c* = 9.703(5) Å, β = 96.94(3)°, *U* = 1649.78 Å^3, *Z* = 2, D_c = 1.445 g cm^{-3}, crystal size = 0.2 × 0.3 × 0.8 mm, Mo-Kα radiation (λ = 0.710 69 Å), *T* = 298 K, *F*(000) = 760, μ = 10.89 cm^{-1}.

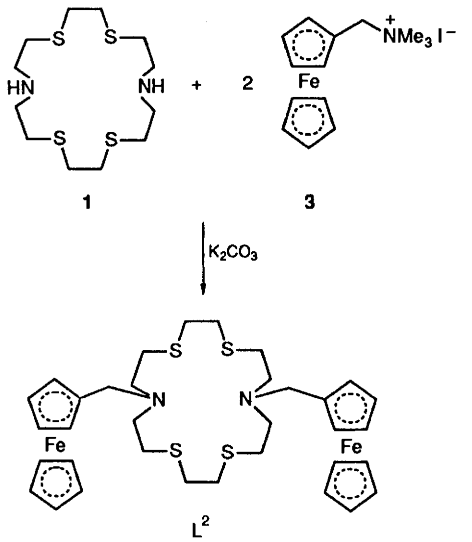
Data collection. 2296 Unique reflections were recorded on a CAD4 diffractometer measuring to θ = 23°. ψ-Scan absorption corrections were made (minimum 0.9527, maximum 0.9950). The structure was solved by Patterson and Fourier methods. The positional and anisotropic vibrational parameters of all non-hydrogen atoms were refined. Hydrogen-atom parameters were refined isotropically.



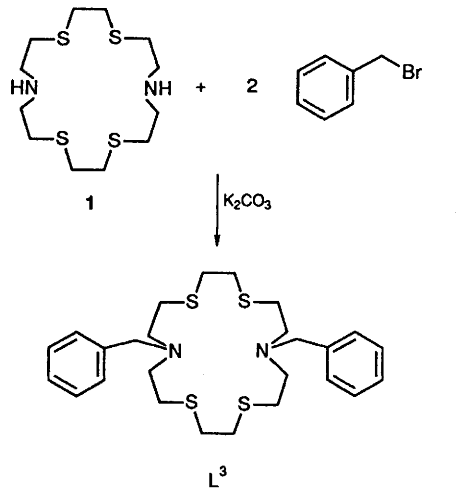
Scheme 1



4



Scheme 2



Scheme 3

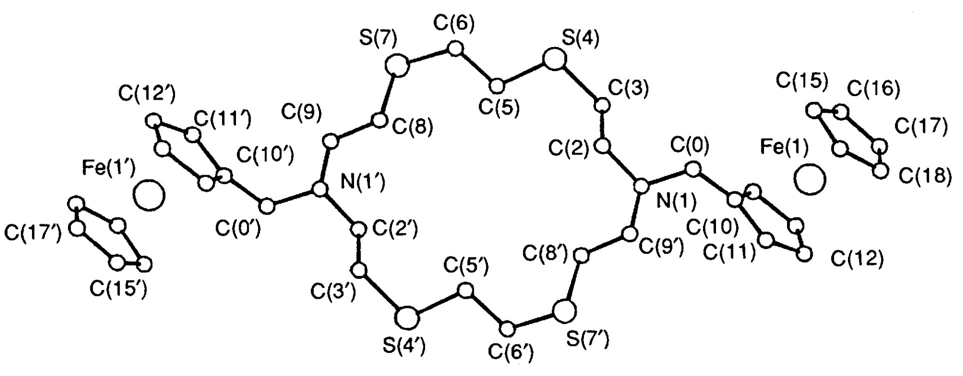


Fig. 2 Structure of ligand L^2

The final R factor was 0.049 for 1442 reflections having $F > 3\sigma(F)$. The fractional coordinates are listed in Table 1, selected bond lengths and angles in Table 2. Programs used as well as sources of scattering-factor data were as in ref. 8.

$[CuL^2]PF_6 \cdot C_{34}H_{46}CuF_6Fe_2N_2PS_4 \cdot 0.33C_6H_{14} \cdot \approx 0.25CH_2Cl_2$, $M \approx 981$, triclinic, space group $P\bar{1}(C_i^1$, no. 2), $a = 21.775(13)$, $b = 20.167(6)$, $c = 18.545(8)$ Å, $\alpha = 62.82(4)$, $\beta = 67.72(4)$, $\gamma = 61.42(4)^\circ$, $U = 6226$ Å^3, $D_c(Z = 6) \approx 1.57$ g cm^{-3}, $F(000) \approx 3031$, $\mu_{Mo} = 14.5$ cm^{-1}, $A^*_{min,max}$ (Gaussian correction) = 1.23, 1.38, specimen (capillary) 0.30 × 0.35 × 0.42 mm, $2\theta_{max} = 40^\circ$, $N = 11\,543$, $N_o[I > 3\sigma(I)] = 8075$, $R,R' = 0.067, 0.075$.

Large block refinement, $n_v = 1350$; statistical reflection weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Anisotropic thermal parameter refinement for non-hydrogen atoms [exceptions: C(336)–C(340) refined isotropically, and solvent fragments, refined as rigid groups]; $(xy,z,U_{iso})_H$ constrained at estimated values. The dichloromethane molecule refined to a population of 0.74$_4$; the hexane population did not differ significantly from unity. One terminal methyl group in the hexane is disordered.

The fractional coordinates are listed in Table 3, selected bond lengths and angles in Tables 4 and 5.

Additional material available for both structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Syntheses.—The macrocyclic ligand, 1,4,10,13-tetrathia-7,16-diazacyclooctadecane **1**, was first synthesised by Black and McLean[5] in 1969 and its co-ordination chemistry, until very recently,[9] has not been fully exploited. The combination of the N_2S_4 donor set invites not only the co-ordination of both 'hard' and 'soft' transition-metal ions but also the possibility of appending ferrocene redox-active moieties to the macrocycle's secondary nitrogen atoms.

The reaction of 2 mol of ferrocenecarbonyl chloride **2**[6] and **1** in the presence of triethylamine gave, after column chromatography, the bis(ferrocenecarbonyl) appended macrocycle L^1 as an orange solid in 64% yield (Scheme 1). Because attempts to reduce the amide linkages using diborane or $LiAlH_4$ failed a new synthetic pathway was devised to synthesise the bis(ferrocenyl) analogue L^2.

Refluxing a mixture of 2 mol of (ferrocenylmethyl)trimethylammonium iodide **3**,[7] **1** and anhydrous potassium carbonate in acetonitrile solution followed by column chromatography gave L^2 in 45% yield as a yellow powdery solid, Scheme 2. This new preparative method of appending metallocene units to secondary nitrogen atoms is a general one and related compounds such as the tetrasubstituted ferrocenyl cyclam derivative **4** have also been successfully synthesised using analogous procedures.[10] The new dibenzyl derivative L^3 was prepared from benzyl bromide and **1** in 95% yield (Scheme 3).

The structures of all these new air-stable compounds were characterised by elemental analyses, mass spectrometry and ^{1}H NMR spectroscopy (see Experimental section).

X-Ray Structural Investigation of Compound L^2.*—Orange crystals of compound L^2 suitable for X-ray structural investigations were obtained from a solution of dichloromethane–methanol (3:1 v/v). The ligand is centrosymmetric and is conformationally expanded. The macrocycle torsion angles are shown in Table 6. If torsional angles of ±60° are classified as *gauche* and those of ±180° as anti it can be seen (Fig. 2) that the ligand possesses two *gauche* C–S–C–C bonds and two anti C–S–C–C bonds, both S–C–C–N and N–C–C–S angles are anti. It is known that the preferential conformation for C–S bonds is *gauche*[11] but that ring strain will force C–S bonds to adopt an anti conformation. For example, in the ligands 1,4,7,10,13,16-hexathiacyclooctadecane, 1,4,7,10-tetrathiacyclododecane and 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane the C–S linkage adopts the *gauche* conformation without exception.[12] In the ligand 1,4,7,10,13-pentathiacyclopentadecane there are two anti C–S bonds, but there is a high degree of ring strain. It appears that the strong anti preference of the N–C–C–S and S–C–C–N bonds in L^2 forces a macrocycle configuration in which two C–S–C–C bonds are necessarily anti, and the four sulphur atoms are exodentate.

Co-ordination Studies.—Copper(II) *complexes.* The green copper(II) complexes $[CuL][BF_4]_2$ where L = L^1, L^2 or L^3 were simply prepared by the addition of copper(II) tetrafluoroborate hexahydrate to room-temperature ethanolic solutions of the appropriate ligand. The complexes were characterised by fast atom bombardment mass spectrometry, infrared spectroscopy, elemental analysis, and room-temperature magnetic susceptibility measurements giving magnetic moments typical for Cu^{2+} (Table 7).

Electronic spectra of L^2 *and of its Copper*(II) *complex.* The electronic spectra of L^2 and its corresponding copper(II) complex, $[CuL^2][BF_4]_2$, were recorded in dichloromethane–acetonitrile (90:10 v/v). A mixed solvent system was used because there was not one solvent in which both ligand and complex were soluble. The visible absorption pattern of the free ligand L^2 was very similar to that of ferrocene itself,[13] however the spectrum of $[CuL^2][BF_4]_2$ exhibited two features of notable interest (Table 8). The band at 620 nm is too intense for an assignment to a d–d metal-ion electronic transition. Similar bands have been observed for many other homoleptic Cu^{2+}–macrocyclic thioether systems and these are thought to arise from a $S \rightarrow Cu^{2+}$ charge-transfer transition.[14]

Compared to the free ligand L^2 the co-ordination of Cu^{2+} also results in a bathochromic shift of the free-ligand band (320 nm) to 380 nm which is also accompanied by an increase in intensity. It is known that bathochromic shifts and intensity enhancement of the band at 325 nm of ferrocene *itself occur* when various electron-withdrawing substituents are attached to the cyclopentadienyl rings.[15] Consequently this spectral observation may be a result of the co-ordinated copper(II) ion perturbing through space the respective electronic energy levels of the appended ferrocenyl redox centres. Indeed, subsequent electrochemical investigations (see below) support this view.

Electrochemical Studies.—The electrochemistry of the parent ligands L^1 and L^2 and of the corresponding copper(II) complexes was investigated using cyclic voltammetry and the results are shown in Tables 9 and 10. Both L^1 and L^2 exhibit one-wave reversible oxidations which suggests that the respective ferrocene moieties present in both ligands become oxidised in one step (Table 9). Detrimental electrode coating thwarted controlled-potential electrolysis experiments to confirm these redox reactions as being two-electron processes. Compared to the free ligands, the oxidation potentials of the corresponding ferrocene–ferrocenium redox couples of the copper(II) complexes are more anodic by 60 and 40 mV respectively (Table 10). This result indicates that the complexed copper(II) cation in the macrocyclic cavity is communicating to the respective covalently appended ferrocene redox centres *via* through-space electronic interactions. The presence of the positively charged guest in the macrocycle destabilises the ferrocenium redox state and consequently an anodic shift of the respective redox couple is observed. Similar anodic shifts of various ferrocene-appended crown ether ligand systems by Group 1A,2A metal guest cations have also been observed.[16–18] Interestingly a very recent publication by Sato *et al.*[19] describes

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* By M. E. Harman and M. B. Hursthouse.

Table 4 Selected bond lengths (Å) for $[CuL^2]PF_6$

N(11)–C(12)	1.46(3)	S(17)–C(18)	1.83(1)
N(11)–C(19′)	1.48(1)	C(18)–C(19)	1.49(3)
N(11)–C(10)	1.46(2)	C(19)–N(11′)	1.44(2)
C(12)–C(13)	1.49(2)	N(11′)–C(12′)	1.45(3)
C(13)–S(14)	1.83(2)	N(11′)–C(10′)	1.50(2)
S(14)–C(15)	1.82(2)	C(12′)–C(13′)	1.51(2)
C(15)–C(16)	1.50(2)	C(13′)–S(14′)	1.83(2)
C(16)–S(17)	1.79(2)	S(14′)–C(15′)	1.82(2)
C(15′)–C(16′)	1.51(2)	C(117)–C(118)	1.40(3)
C(16′)–S(17′)	1.82(2)	C(118)–C(119)	1.40(3)
S(17′)–C(18′)	1.82(1)	C(10′)–C(110′)	1.49(2)
C(18′)–C(19′)	1.46(3)	C(110′)–C(111′)	1.40(3)
C(10)–C(110)	1.51(2)	C(110′)–C(114′)	1.41(3)
C(110)–C(111)	1.41(2)	C(111′)–C(112′)	1.39(2)
C(110)–C(114)	1.41(2)	C(112′)–C(113′)	1.36(3)
C(111)–C(112)	1.42(2)	C(113′)–C(114′)	1.46(2)
C(112)–C(113)	1.44(2)	C(115′)–C(116′)	1.38(3)
C(113)–C(114)	1.38(2)	C(115′)–C(119′)	1.38(6)
C(115)–C(116)	1.40(3)	C(116′)–C(117′)	1.38(5)
C(115)–C(119)	1.39(3)	C(117′)–C(118′)	1.35(5)
C(116)–C(117)	1.37(3)	C(118′)–C(119′)	1.41(5)

Table 5 Selected bond angles (°) for $[CuL^2]PF_6$

C(12)–N(11)–C(19′)	111(1)	C(12′)–C(13′)–S(14′)	107(1)
C(12)–N(11)–C(10)	112(1)	Cu–S(14′)–C(13′)	109.3(7)
C(19′)–N(11)–C(10)	109(1)	Cu–S(14′)–C(15′)	99.9(7)
N(11)–C(12)–C(13)	113(1)	C(13′)–S(14′)–C(15′)	97.9(7)
C(12)–C(13)–S(14)	109(1)	S(14′)–C(15′)–C(16′)	114(1)
Cu–S(14)–C(13)	110.7(5)	C(15′)–C(16′)–S(17′)	113(1)
Cu–S(14)–C(15)	99.0(6)	Cu–S(17′)–C(16′)	96.4(4)
C(13)–S(14)–C(15)	100.6(8)	Cu–S(17′)–C(18′)	113.6(4)
S(14)–C(15)–C(16)	115(1)	C(16′)–S(17′)–C(18′)	102.0(8)
C(15)–C(16)–S(17)	115(1)	S(17′)–C(18′)–C(19′)	113(1)
Cu–S(17)–C(16)	96.1(5)	N(11)–C(19′)–C(18′)	113(1)
Cu–S(17)–C(18)	113.6(5)	N(11)–C(10)–C(110)	113(1)
C(16)–S(17)–C(18)	101.4(8)	Fe(1)–C(110)–C(10)	128(1)
S(17)–C(18)–C(19)	114(1)	Fe(1)–C(110)–C(111)	69(1)
C(18)–C(19)–N(11′)	111(1)	Fe(1)–C(110)–C(114)	70(1)
C(19)–N(11′)–C(12′)	113(1)	C(10)–C(110)–C(111)	125(1)
C(19)–N(11′)–C(10′)	112(1)	C(10)–C(110)–C(114)	128(1)
C(12′)–N(11′)–C(10′)	111(1)	C(111)–C(110)–C(114)	107(1)
N(11′)–C(12′)–C(13′)	113(1)		

Table 6 Macrocycle torsion angles (°) for the parent ligand L^2 (N, S are italicized)

9–*1*–2–3	−77.7(8)	5–6–7–8	167.4(6)
1–2–3–*4*	174.2(5)	6–7–8–9	86.2(7)
2–3–*4*–5	−179.2(7)	7–8–9–*1*	−175.5(5)
3–*4*–5–6	63.5(7)	8–9–*1*–2	(±)156.9(6)
4–5–6–7	128.8(9)		

Table 7 Characterisation of copper(II) complexes

Complex	Colour	μ*	Yield (%)
$[CuL^1][BF_4]_2$	Apple-green	1.96	37
$[CuL^2][BF_4]_2$	Emerald-green	1.82	45
$[CuL^3][BF_4]_2$	Pale green	2.26	31

* Error ±0.1.

Table 8 Electronic spectral data[a]

Compound	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
L^2	434	2.2×10^4
	320	1.8×10^4
$[CuL^2][BF_4]_2$	620	3.5×10^4
	380[b]	1.2×10^5

[a] Solvent dichloromethane–acetonitrile (90:10 v/v). [b] Shoulder.

Table 9 Electrochemical data for ligands L^1 and L^2

Compound	$E_{\frac{1}{2}}$[a]/V	ΔE_p[b]/mV
L^1	+0.48	100 (90)
L^2	+0.66	80 (100)

[a] Obtained in acetonitrile solution containing 0.2 mol dm^{-3} $[NBu^n{}_4][BF_4]$ as supporting electrolyte. Solutions were *ca.* 2×10^{-3} mol dm^{-3} in compound, and potentials were determined with reference to the SCE. Scan rate 0.2 V s^{-1}, 21 °C. [b] Difference between anodic and cathodic peak potentials. The values for ferrocene are in parentheses.

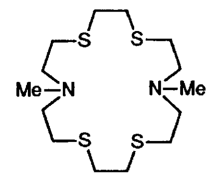
Table 10 Electrochemical data for the copper(II) complexes

Complex	Ferrocenyl[a] $\Delta E_{\frac{1}{2}}$/V	Copper(II)–copper(I)[a] E_{Pa}[b]/V	E_{Pc}[c]/V
$[CuL^1][BF_4]_2$	+0.72	−0.17	−0.39
$[CuL^2][BF_4]_2$	+0.52	−0.11	−0.26
$[CuL^3][BF_4]_2$	—	−0.15	−0.38

[a] Obtained in acetonitrile solution containing 0.2 mol dm^{-3} $[NBu^n{}_4][BF_4]$ as supporting electrolyte. Solutions were *ca.* 2×10^{-3} mol dm^{-3} in compound, and potentials determined with reference to the SCE. Scan rate 0.2 V s^{-1}, 21 °C. [b] Anodic peak potential. [c] Cathodic peak potential.

the spontaneous reduction of initially co-ordinated copper(II) to copper(I) and concomitant oxidation of ferrocene to ferrocenium on addition of $Cu(BF_4)_2$ to polythia[*n*]ferrocenophanes.

The copper(II)–copper(I) redox couples, shown in Table 10, are all quasi-reversible and are of similar potentials to those of the reversible copper(II)–copper(I) couple reported by Schröder and co-workers[20] for the $[CuL][BF_4]_2$ complex (L = compound 1). However, the same group have recently reported a more anodic couple at +0.18 V (*versus* SCE) for the corresponding complex of the *N*-methyl ligand **5** and suggest for possible steric reasons a much greater interaction of the copper(II) cation with the soft thioether sulphur donors of the macrocycle is responsible for stabilising the copper(I) redox state.[20]



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Copper(I) *Complex of* L^2.—The copper(I) complex $[CuL^2]PF_6$ was prepared by the addition of a dry acetonitrile solution of $[Cu(MeCN)_4]PF_6$[21] to an equimolar dichloromethane solution of L^2. Removal of the solvent *in vacuo* and recrystallisation from dichloromethane–acetonitrile (1:2) gave the complex as an orange solid in moderate yield. The complex was characterised by elemental analyses, ^1H, ^{13}C NMR and fast atom bombardment mass spectroscopy. A comparison of the ^1H NMR spectra of the ligand L^2 and $[CuL^2]PF_6$ revealed that large downfield shifts of up to 0.2 ppm for the macrocyclic ring protons result on co-ordination of the copper(I) ion. However the cyclopentadienyl ring protons of the respective ferrocenyl moieties were virtually unaffected ($\Delta\delta$ < 0.03 ppm) by complexation. Analogous observations were also observed in the respective ^{13}C NMR spectra.

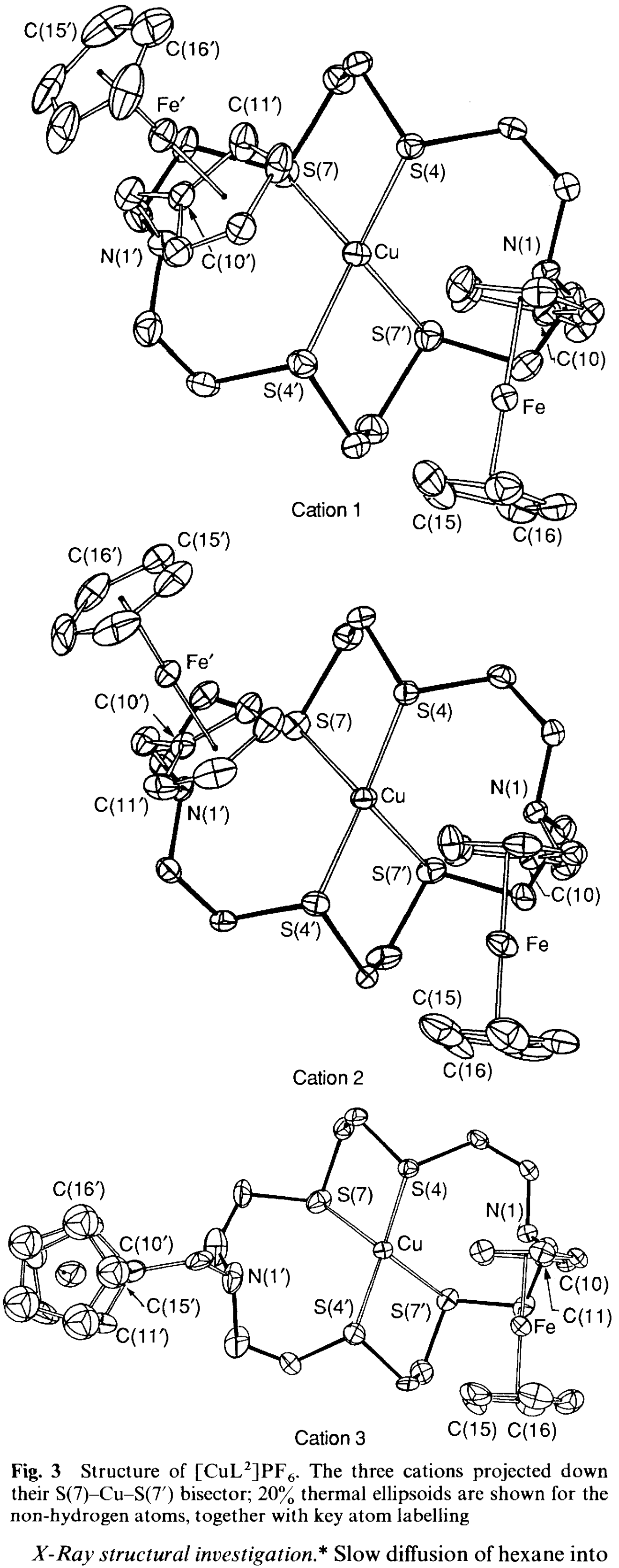

Fig. 3 Structure of [CuL^2]PF$_6$. The three cations projected down their S(7)–Cu–S(7′) bisector; 20% thermal ellipsoids are shown for the non-hydrogen atoms, together with key atom labelling

Table 11 Copper atom environments (distances in Å, angles in °)

	Molecule		
	1	2	3
Cu–S(4)	2.266(5)	2.276(5)	2.291(5)
Cu–S(4′)	2.279(6)	2.280(6)	2.285(7)
Cu–S(7)	2.349(5)	2.347(4)	2.326(5)
Cu–S(7′)	2.369(4)	2.359(3)	2.347(4)
Cu ··· Fe	5.781(4)	5.809(4)	5.843(4)
Cu ··· Fe′	6.234(3)	6.322(3)	7.802(5)
S(4) ··· S(7)	3.372(5)	3.375(5)	3.355(5)
S(4′) ··· S(7′)	3.373(6)	3.395(6)	3.355(6)
S(4) ··· S(7′)	4.083(6)	4.115(5)	4.085(5)
S(4′) ··· S(7)	4.065(8)	4.057(7)	4.008(8)
S(4) ··· S(4′)	3.998(8)	4.015(8)	4.007(8)
S(7) ··· S(7′)	3.633(6)	3.532(5)	3.724(6)
S(4)–Cu–S(4′)	123.2(2)	123.5(2)	123.5(2)
S(7)–Cu–S(7′)	100.7(1)	97.3(1)	105.7(1)
S(4)–Cu–S(7′)	123.5(2)	125.2(2)	122.2(2)
S(4′)–Cu–S(7)	122.9(2)	122.5(2)	120.7(2)
S(4)–Cu–S(7)	93.9(2)	93.8(2)	93.2(2)
S(4′)–Cu–S(7′)	93.0(2)	94.1(2)	92.8(2)

Table 12 Macrocycle torsion angles (°) for the copper(I) complex [CuL^2]PF$_6$

	Molecule					
	1	1′	2	2′	3	3′
9-*1*-2-3	77(1)	77(1)	77(1)	75(1)	77(1)	89(2)
1-2-3-*4*	59(1)	62(1)	59(1)	63(1)	59(1)	45(2)
2-3-*4*-5	175(1)	173(1)	179(1)	174(1)	171(1)	173(2)
3-*4*-5-6	80(1)	76(1)	81(1)	77(1)	77(1)	74(2)
4-5-6-*7*	56(1)	58(1)	56(1)	56(1)	56(1)	57(2)
5-6-*7*-8	73(1)	72(1)	71(1)	74(1)	72(1)	78(1)
6-*7*-8-9	−153(1)	−151(1)	−155(1)	−147(1)	−161(1)	−152(1)
7-8-9-*1*	76(1)	76(1)	79(1)	74(1)	79(2)	79(1)
8-9-*1*-2	−153(1)	−155(1)	−154(1)	−157(1)	−141(2)	−156(1)

Atoms N, S are italicised.

*X-Ray structural investigation.** Slow diffusion of hexane into a dilute dichloromethane solution of [CuL^2]PF$_6$ gave orange crystals for X-ray structural investigation. The asymmetric unit of the structure comprises three different macrocyclic configurations (Fig. 3) accompanied by solvent components modelled as 0.75 dichloromethane and a fully populated hexane. The copper(I) ion environments are shown in Table 11. It can be seen that the copper(I) ion possesses a distorted-tetrahedral geometry with the Cu–S(4) and Cu–S(4′) bonds being on average some 0.09 Å shorter than the Cu–S(7) and Cu–S(7′) bonds. This distorted-tetrahedral array is not unusual in the copper(I) complexes of macrocyclic thioethers. The complexes of 1,4,7,10,13-pentathiacyclopentadecane[22] and 1,4,8,11-tetrathiocyclotetradecane[23] also show a distorted-tetrahedral geometry for copper(I). The three independent copper(I) environments are very similar; this similarity extends to the ring conformation. These are shown in Table 12.

As in the parent ligand there are two *gauche* and two anti C–S–C–C bonds but there are two *gauche* N–C–C–S bonds (the parent ligand has two anti N–C–C–S bonds). However, the C–S bonds which were *gauche* in the ligand L^2 are now anti and *vice versa*.

The consistent disposition of ferrocene 1 in all three copper(I) cations is suggestive of a preferred orientation. This is not maintained, however, for ferrocene 1′ which has different but similar positions in cations 1 and 2 and uniquely new dispositions in cation 3 and the free ligand. These widely varying dispositions do not appear to influence the macrocyclic configuration. The Cu ··· Fe distances vary between 5.781 and 7.802 Å but these probably represent extremes of the possible range.

Conclusion

Novel redox-active bis(ferrocenecarbonyl) and bis(ferrocenyl) derivatives L^1 and L^2 of the macrocycle **1** have been prepared

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* By M. I. Ogden and A. H. White.

and their corresponding copper-(II) and -(I) complexes isolated. Electrochemical studies reveal that the respective ferrocene–ferrocenium redox couples of ligands L^1 and L^2 are perturbed to more anodic potentials by up to 60 mV on co-ordination of the copper(II) ion. These copper(II) complexes also exhibit quasi-reversible copper(II)–copper(I) redox couples at negative potentials (≈ -0.2 V) *versus* SCE. The co-ordination chemistry of L^1 and L^2 and related ligands with transition metals of catalytic interest is currently being studied.

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