Ammonium Redox-responsive Receptors containing Multiple Ferrocene and Quinone Redox-active Centres attached to Di- and Tri-aza Crown Ether Macrocycles†

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Eight new redox-active di- and tri-aza crown ether macrocyclic ligands containing multiple ferrocene and quinone moieties have been prepared, including the first reported mixed ferrocene–quinone macrocyclic ligand. Solution ^1H and ^{13}C NMR complexation studies suggest these ligands form 1:1 stoichiometric complexes with ammonium as guest cation. Single-crystal structures of the hydrogen hexafluorophosphate salt of 7,16-bis(ferrocenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane and the ammonium complex of 4,10,16-tris(ferrocenylmethyl)-1,7,13-trioxa-4,10,16-triazacyclooctadecane have also been determined. Electrochemical investigations reveal the respective ferrocene–ferrocenium redox couples of most of the ligands are perturbed to more positive potentials on co-ordination of NH_4^+ and K^+ guest cations. The above tris(ferrocenylmethyl) ligand selectively binds and electrochemically recognises NH_4^+ in the presence of equimolar concentrations of K^+. Secondary amide-linked ferrocene aza crown ether ligands electrochemically sense the NH_4^+ guest cation primarily *via* host ferrocenecarboxide carbonyl oxygen–H–NH_3^+ hydrogen-bonding electrostatic interactions.

In pursuit of advancing chemical sensor technology,[1] considerable interest is being shown in the syntheses of redox-active macrocyclic receptor molecules which contain a redox centre in close proximity to a metal cation binding site.[2–6] These systems can be designed to recognise electrochemically the binding of a metal guest cation either through space interactions or *via* various bond linkages between the receptor site and redox centre.[2] In contrast to the alkali-metal co-ordination studies of electrochemically reducible[3,5,7] and oxidisable[4,6,8–11] redox-active macrocycles, the design and syntheses of prototype amperometric ammonium cation sensor systems have yet to be reported. This paper describes the syntheses of new redox-active di- and tri-aza crown ether macrocycles L^1–L^8 containing multiple ferrocene and quinone moieties including the X-ray structural studies of one ligand and of an ammonium complex, and demonstrates by use of electrochemical techniques for the first time that ammonium guest cation binding at the aza crown ether recognition sites perturbs the redox potential of the ferrocene–ferrocenium couple. A preliminary report of this work has appeared.[12]

Experimental

Reactions were carried out under an atmosphere of dry nitrogen and solvents were distilled prior to use from an appropriate drying agent. Proton NMR spectra were recorded at 400 and 270 MHz and ^{13}C NMR spectra at 100 and 67.8 MHz using tetramethylsilane as internal standard. Microanalyses were performed by the Inorganic Chemistry Laboratory, Oxford and by the Birmingham University Chemistry Department microanalytical service. Electrochemical measurements were performed using a PAR 174A polarographic analyser. Cyclic voltammetric measurements were carried out in acetonitrile solution containing 0.2 mol dm^{-3} $NBu^n{}_4BF_4$ or saturated NMe_4Cl as supporting electrolyte using a platinum-bead working electrode with ferrocene as internal reference. Values are quoted relative to the saturated calomel reference electrode (SCE). Positive-ion fast-atom-bombardment (FAB) mass spectrometry was performed using a primary atom beam of argon (6 keV, *ca.* 9.6 × 10^{-16} J) on a Kratos MS80 RF mass spectrometer coupled to a DS55 data system.

1,7,13-Trioxa-4,10,16-triazacyclooctadecane (triaza-18-crown-6) **1**,[14] chlorocarbonylferrocene **2**,[15] trimethylammoniomethylferrocene iodide **3**,[16] 4-toluene-*p*-sulfonyl-1,7,13-trioxa-4,10,16-triazacyclooctadecane **8**[14] and 2-bromomethylanthraquinone **7**[17] were prepared according to literature procedures.

Syntheses.—4,10,16-*Tris(ferrocenylcarbonyl)*-1,7,13-*trioxa*-4,10,16-*triazacyclooctadecane* L^1. Chlorocarbonylferrocene **2** (0.39 g, 1.57 mmol) was dissolved in dry toluene (80 cm^3) and transferred to a pressure-equalising dropping funnel (100 cm^3). This solution was added, over 3 h, to a stirred solution of compound **1** (0.13 g, 0.5 mmol), triethylamine (0.21 g, 1.5 mmol) and a microspatula of 4-dimethylaminopyridine in dry toluene (80 cm^3) under nitrogen. The solution was refluxed for 4 h and the solvent then removed *in vacuo*. The residue was redissolved in dichloromethane (80 cm^3) and water (80 cm^3) and the aqueous layer was extracted with dichloromethane (3 × 40 cm^3). The organic extracts were dried ($MgSO_4$), filtered and evaporated to dryness. The orange residue was purified by column chromatography on alumina, eluting the product with dichloromethane–methanol (99.5:0.5, v/v). Recrystallisation from diethyl ether–hexane gave L^1 as an orange solid (0.34–0.38 g, 76–85% yield), m.p. 55–57 °C. IR 1615 cm^{-1} (C=O stretch). FAB: *m/z* 898, *M* + H. ^1H NMR ($CDCl_3$): δ 3.72–3.90 (24 H, m, OCH_2 + NCH_2), 4.22 (15 H, s), 4.33–4.48 (6 H, m) and 4.64–4.72 (6 H, m) (all ferrocene H) (Found: C, 60.4; H, 4.6; N, 6.2. Calc. for $C_{45}H_{51}Fe_3N_3O_6$: C, 60.2; H, 4.7; N, 5.7%).

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4,10,16-*Tris(ferrocenylmethyl)*-1,7,13-*trioxa*-4,10,16-*triazacyclooctadecane* L^2. Compound **3** (0.30 g, 0.78 mmol) was dissolved in dry acetonitrile (60 cm^3) and transferred to a pressure-equalising dropping funnel (100 cm^3). This solution was added, over 1 h, to a mixture of **1** (0.05 g, 0.19 mmol) and potassium carbonate (0.26, 1.88 mol) in dry acetonitrile (50 cm^3) under nitrogen. The resulting mixture was further refluxed for 48 h, the potassium carbonate filtered off and washed with acetonitrile, and the solvent evaporated off. The resultant orange residue was dissolved in dichloromethane (60 cm^3) and water (50 cm^3) and the aqueous layer extracted with dichloromethane (3 × 40 cm^3). The organic extracts were dried ($MgSO_4$), filtered, and evaporated to dryness. The product was purified by alumina column chromatography using dichloromethane–methanol (99.5:0.5, v/v) as eluent to give L^2 as an orange solid (0.14 g, 86% yield). FAB: *m/z* 856, *M* + H. NMR ($CDCl_3$): ^1H, δ 2.6–2.75 (12 H, m, CH_2N), 3.40–3.55 (18 H, m, $CH_2O + CH_2$ bound to ferrocene, 4.10–4.25 (27 H, m, ferrocene H) and 5.34 (4 H, s, CH_2Cl_2); ^{13}C, δ 54.1, 55.5, 68.7, 69.3, 70.3 and 71.0 (Found: C, 55.8; H, 6.2; N, 3.4. Calc. for $C_{45}H_{57}Fe_3N_3O_3 \cdot 2CH_2Cl_2$: C, 55.1; H, 6.0; N, 4.0%).

7,16-*Bis(ferrocenylmethyl)*-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* L^3. The procedure for the preparation of L^3 followed that described for L^2, replacing **1** with 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (diaza-18-crown-6) **4** and the reflux time was reduced from 48 to 24 h. The product was purified by alumina column chromatography with dichloromethane–methanol (98:2, v/v) as eluent to give **3** as an orange solid (70% yield), m.p. 109–111 °C. FAB: *m/z* 659, *M* + H. NMR ($CDCl_3$): ^1H, δ 2.60–2.80 (8 H, m, NCH_2), 3.50–3.70 (20 H, m, $OCH_2 + CH_2$ bound to ferrocene) and 4.06–4.25 (18 H, m, CH_2O + ferrocene H); ^{13}C, δ 54.1, 55.4, 68.6, 69.3, 70.5, 71.0 and 71.2 (Found: C, 60.3; H, 6.9; N, 4.0. Calc. for $C_{34}H_{46}Fe_2N_2O_4$: C, 61.0; H, 7.0; N, 4.3%).

The salt $[H_2L^3][PF_6]_2$ was prepared by dissolving L^3 in dilute hydrochloric acid and subsequently adding an excess of NH_4PF_6. The precipitated product was recrystallised from ethanol–acetone (Found: C, 42.5; H, 5.1; N, 2.5. Calc. for $C_{34}H_{48}F_{12}Fe_2N_2O_4P_2$: C, 43.0; H, 5.1; N, 2.9%).

4,10,16-*Tris(3-aminopropyl)*-1,7,13-*trioxa*-4,10,16-*triazacyclooctadecane* **5**. Compound **1** (0.25 g, 0.96 mmol) was dissolved in acrylonitrile (100 cm^3) and the resulting solution refluxed for 48 h under nitrogen. The product was evaporated under reduced pressure and the residual oil purified by column chromatography on alumina using dichloromethane–ethanol (40:1, v/v) as eluent to give 4,10,16-tris(2-cyanoethyl)-1,7,13-trioxa-4,10,16-triazacyclooctadecane as a colourless oil (0.32–0.38 g, 80–94% yield). IR 2250 cm^{-1} (CN stretch). FAB: *m/z* 421, *M* + H. ^1H NMR ($CDCl_3$): δ 2.47–2.52 (6 H, m, NCH_2CH_2CN), 2.78–2.96 (18 H, m, $CH_2CN + CH_2N$), 3.35 (3 H, s, CH_3), 3.53–3.76 (12 H, m, CH_2O) and 4.10 (1 H, br s, OH) (Found: C, 57.8; H, 8.8; N, 18.6. Calc. for $C_{21}H_{36}N_6O_3 \cdot CH_3OH$: C, 58.3; H, 8.8; N, 18.6%).

The trinitrile (0.16 g, 0.38 mmol) was treated with diborane–tetrahydrofuran (1 mol dm^{-3}, 50 cm^3) at 0 °C under nitrogen *via* syringe and the solution heated under reflux for 48 h. The mixture was cooled to room temperature, the excess of diborane was destroyed by careful dropwise addition of ice-cold water (*ca.* 2.0 cm^3) and the solution was evaporated to give the crystalline amine–borate adduct. The adduct was heated under reflux for 24 h in 6 mol dm^{-3} hydrochloric acid (60 cm^3), the resulting aqueous solution was evaporated and the residual hydrochloric salt converted into the free base using a Dowex 1 × 8–100 (50–100 mesh) ion-exchange resin. Compound **5** was obtained as a colourless oil (0.14–0.16 g, 85–97% yield). IR 3350 cm^{-1} (NH stretch). FAB: *m/z* 432, *M* + H. ^1H NMR ($CDCl_3$): δ 1.55–1.68 (6 H, m, $NCH_2CH_2CH_2NH_2$), 1.82 (6 H, br s, NH), 2.52–2.65 (24 H, m, CH_2N) and 3.55–3.66 (12 H, m, CH_2O).

7,16-*Bis(3-aminopropyl)*-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* **6**. The procedure for the preparation of compound **6** followed that described for **5**. The dinitrile was a colourless oil (80–85% yield). IR 2250 cm^{-1} (CN stretch). FAB: *m/z* 369, *M* + H. ^1H NMR ($CDCl_3$): δ 2.55–2.60 (4 H, m, NCH_2CH_2CN), 2.75–2.92 (12 H, m, CH_2N), 3.31 (1.5 H, s, CH_3), 3.53–3.70 (16 H, m, CH_2O) and 4.02 (0.5 H, br s, OH) (Found: C, 57.4; H, 8.5; N, 14.5. Calc. for $C_{18}H_{32}N_4O_4 \cdot 0.5CH_3OH$: C, 57.3; H, 8.8; N, 14.9%).

The diamine **6** was obtained as a colourless oil (84–98% yield). IR 3350 cm^{-1} (NH stretch). FAB: *m/z* 377, *M* + H. ^1H NMR ($CDCl_3$): δ 1.60–1.80 (4 H, m, $NCH_2CH_2CH_2NH_2$), 1.90 (4 H, br s, NH), 2.50–2.70 (16 H, m, NCH_2) and 3.60–3.65 (16 H, m, CH_2O).

4,10,16-*Tris(3-ferrocenecarboxamidepropyl)*-1,7,13-*trioxa*-4,10,16-*triazacyclooctadecane* L^4. Chlorocarbonylferrocene **2** (1.2 g, 4.80 mmol) was dissolved in dry dichloromethane (45 cm^3) and transferred to a pressure-equalising dropping funnel (100 cm^3). This solution was added, over 4 h, to a stirred solution of triamine **5** (0.20 g, 0.46 mmol), triethylamine (0.2 cm^3, 3.96 mmol) and a microspatula of 4-dimethylaminopyridine in dry dichloromethane under nitrogen. The solution was stirred overnight and then evaporated *in vacuo*. The resulting orange residue was redissolved in dichloromethane (60 cm^3) and water (50 cm^3) and the aqueous layer extracted with dichloromethane (3 × 40 cm^3). The organic extracts were dried ($MgSO_4$), filtered and evaporated to dryness. The product was purified by column chromatography on alumina using dichloromethane–methanol (98:2, v/v) as eluent to give L^4 as an orange oil (0.28–0.34 g, 57–69% yield). IR 1620 (C=O stretch), 3300 cm^{-1} (NH stretch). FAB: *m/z* 1069, *M* + H. ^1H NMR ($CDCl_3$): δ 1.65–1.75 (6 H, m, $NCH_2CH_2CH_2NHCO$), 2.61–2.79 (18 H, m, NCH_2), 3.32 (3 H, s, CH_3), 3.46–3.70 (18 H, m, $CH_2O + CH_2NHCO$), 4.06 (1 H, br s, OH), 4.20 (15 H, s), 4.32–4.39 (6 H, m) and 4.63–4.75 (6 H, m) (all ferrocene H) and 5.75 (3 H, br s, NH) (Found: C, 58.5; H, 6.7; N, 6.7. Calc. for $C_{54}H_{72}Fe_3N_6O_6 \cdot CH_3OH$: C, 59.4; H, 7.1; N, 7.4%).

7,16-*Bis(3-ferrocenecarboxamidopropyl)*-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* L^5. The procedure for preparation of L^5 followed that described for L^4, replacing triamine **5** with diamine **6** to give an orange oil (55–65% yield). FAB: *m/z* 801, *M* + H. IR 1620 (C=O stretch), 2250 (CN stretch), 3300 cm^{-1} (NH stretch). NMR ($CDCl_3$): ^1H, δ 1.60–1.80 (4 H, m, $NCH_2CH_2CH_2NHCO$), 2.62–2.80 (12 H, m, NCH_2), 3.30 (6 H, s, CH_3), 3.40–3.75 (20 H, m, $CH_2 + CH_2NHCO$), 4.01 (2 H, br s, OH), 4.22 (10 H, s), 4.29–4.39 (4 H, m) and 4.62–4.73 (4 H, m) (all ferrocene H) and 5.70 (2 H, br s, NH); ^{13}C, δ 26.2, 38.5, 53.3, 54.0, 68.3, 69.3, 69.7, 70.2, 70.3, 76.7 and 170.5 (Found: C, 58.3; H, 7.4; N, 6.4. Calc. for $C_{40}H_{56}Fe_2N_4O_6 \cdot 2CH_3OH$: C, 58.6; H, 7.8; N, 5.9%).

7,16-*Bis[3-bis(ferrocenylmethyl)aminopropyl]*-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* L^6. The procedure for the preparation of L^6 followed that described for L^2, replacing compound **1** with diamine **6**. The reflux time was increased from 48 to 72 h and the product was purified by alumina column chromatography with dichloromethane–methanol (97:3, v/v) as eluent to give L^6 as an orange oil (92% yield). FAB: *m/z* 1169, *M* + H. ^1H NMR ($CDCl_3$): δ 1.60–1.71 (4 H, m, $NCH_2CH_2CH_2N$), 2.75–2.90 (16 H, m, CH_2N), 3.59–3.75 (20 H, m, $CH_2O + CH_2$ bound to ferrocene), 4.10–4.26 (36 H, m, ferrocene H) and 5.34 (4 H, s, CH_2Cl_2) (Found: C, 56.8; H, 6.0; N, 3.5. Calc. for $C_{62}H_{80}Fe_4N_4O_4 \cdot 2CH_2Cl_2$: C, 57.4; H, 6.3; N, 4.2%).

4,10,16-*Tris(9,10-dioxoanthracen-2-ylmethyl)*-1,7,13-*trioxa*-4,10,16-*triazacyclooctadecane* L^7. To a refluxing mixture of compound **1** (0.08 g, 0.32 mmol) and potassium carbonate (0.44 g, 3.17 mmol) in dry acetonitrile (50 cm^3), under nitrogen, was added, over 2 h 2-bromomethylanthraquinone **7** (0.29 g, 0.96 mmol) in dry acetonitrile (60 cm^3). The mixture was refluxed for 24 h, the potassium carbonate filtered off and washed with acetonitrile, and the solvent evaporated off. The brown oily residue was redissolved in dichloromethane (70 cm^3) and water (50 cm^3). The aqueous layer was extracted with dichloromethane (3 × 50 cm^3) and the organic layer was dried ($MgSO_4$), filtered and evaporated to dryness. Purification by alumina column chromatography using dichloromethane–methanol (98:2, v/v) as eluent gave L^7 as a pale brown solid after recrystallisation from ethanol (0.16 g, 55% yield), m.p. 95–97 °C. IR 1670 cm^{-1} (C=O stretch). FAB: *m/z* 922, *M* + H. ^{1}H NMR ($CDCl_3$): δ 2.75–2.90 (12 H, m, CH_2N), 3.55–3.70 (12 H, m, CH_2O), 3.90 (6 H, s, CH_2O), 5.35 (2 H, s, CH_2Cl_2) and 7.70–8.30 (21 H, m, quinone H) (Found: C, 69.3; H, 5.5; N, 4.5. Calc. for $C_{57}H_{51}N_3O_9{\cdot}CH_2Cl_2$: C, 69.2; H, 5.5; N, 4.2%).

4,10-*Bis(ferrocenylmethyl)*-16-*toluene*-p-*sulfonyl*-1,7,13-*trioxa*-4,10,16-*triazacyclooctadecane* **9**. Trimethylaminomethylferrocene iodide **3** (0.22 g, 0.57 mmol) was dissolved in dry acetonitrile (60 cm^3) and transferred to a pressure-equalising dropping funnel (100 cm^3). This solution was added, over 4 h, to a stirred mixture of compound **8** (0.10 g, 0.24 mmol) and potassium carbonate (0.33 g, 2.4 mmol) in dry acetonitrile (50 cm^3), under nitrogen. This mixture was refluxed for 24 h, the potassium carbonate filtered off and washed with acetonitrile and the solvent evaporated to dryness. The orange residue was redissolved in dichloromethane (80 cm^3) and water (60 cm^3) and the aqueous layer extracted with dichloromethane (3 × 50 cm^3). The organic extracts were dried ($MgSO_4$), filtered and evaporated to dryness to leave compound **9** as an orange oil (0.17 g, 87% yield). FAB: *m/z* 812, *M* + H. ^{1}H NMR ($CDCl_3$): δ 2.41 (3 H, s, tosyl methyl) 2.69–2.87 (8 H, m, CH_2N), 3.45–3.67 (20 H, m, CH_2O + CH_2N bound to tosyl + CH_2 bound to ferrocene), 4.15–4.26 (18 H, m, ferrocene H) and 7.24–7.71 (4 H, d, *J* = 8.0 Hz, tosyl H).

4,10-*Bis(ferrocenylmethyl)*-1,7,13-*trioxa*-4,10,16-*triazacyclooctadecane* **10**. To a stirred suspension of lithium aluminium hydride (0.16 g, 42 mmol) in dry tetrahydrofuran (thf) (25 cm^3) was added, under nitrogen, a solution of compound **9** (0.17 g, 0.21 mmol) in dry thf (15 cm^3). The resulting mixture was refluxed for 36 h and then allowed to cool to room temperature. Water (*ca.* 12 cm^3) was added and the mixture filtered through Celite. The filtrate was evaporated to dryness, and redissolved in dichloromethane (80 cm^3) and water (50 cm^3). The aqueous layer was extracted with dichloromethane (4 × 40 cm^3), and the organic extracts were dried ($MgSO_4$), filtered, and evaporated to dryness to leave compound **10** as a pale yellow oil (0.13 g, 94% yield). IR 3350 cm^{-1} (NH stretch). FAB: *m/z* 658, *M* + H. ^{1}H NMR ($CDCl_3$): δ 2.20 (1 H, br s, NH), 2.60–2.85 (12 H, m, CH_2N), 3.60–3.75 (16 H, m, CH_2O + CH_2 bound to ferrocene), 4.10–4.20 (18 H, m, ferrocene H) and 5.35 (2 H, s, CH_2Cl_2) (Found: C, 56.1; H, 6.2; N, 5.2. Calc. for $C_{34}H_{47}Fe_2N_3O_3{\cdot}CH_2Cl_2$: C, 56.6; H, 6.6; N, 5.7%).

4-(9,10-*Dioxoanthracen*-2-*ylmethyl*)-10,16-*bis(ferrocenylmethyl)*-1,7,13-*trioxa*-4,10,16-*triazacyclooctadecane* L^8. The procedure for the preparation of L^8 followed that described for L^7, replacing compound **1** with **10**. The compound was obtained as an orange oil (38% yield). IR 1670 cm^{-1} (C=O stretch). FAB: *m/z* 878, *M* + H. ^{1}H NMR ($CDCl_3$): δ 2.60–2.80 (12 H, m, CH_2N), 3.55–3.80 (16 H, m, CH_2O + CH_2 bound to ferrocene), 4.10–4.25 (18 H, m, ferrocene H), 5.33 (2 H, s, CH_2Cl_2) and 7.75–8.40 (7 H, m, quinone H) (Found: C, 61.1; H, 6.7; N, 3.7. Calc. for $C_{49}H_{55}Fe_2N_3O_5{\cdot}CH_2Cl_2$: C, 62.4; H, 6.0; N, 4.4%).

Structure Determinations.—Crystal data. $[H_2L^3][PF_6]_2{\cdot}2EtOH$, $C_{38}H_{60}F_{12}Fe_2N_2O_6P_2$, $M = 1044.2$, triclinic, space group $P\bar{1}$, $a = 12.877(15)$, $b = 10.299(13)$, $c = 10.582(12)$ Å, $\alpha = 87.9(1)$, $\beta = 114.9(1)$, $\gamma = 115.4(1)°$, $U = 1132.4$ Å^3, $D_m = 1.48$ g cm^{-3}, $Z = 1$, $D_c = 1.52$ g cm^{-3}, $\lambda = 0.7107$ Å, $\mu = 9.33$ cm^{-1}, $F(000) = 548$.

A crystal of approximate size 0.30 × 0.30 × 0.30 mm was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were collected *via* variable-width ω scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 3540 Independent reflections were measured with a 2θ maximum of 50° of which 2098 with $I > 2\sigma(I)$ were used in subsequent refinement. No deterioration in the crystal was observed during the data collection. The structure was determined by the heavy-atom method and all atoms were then located by Fourier methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined isotropically. The weighting scheme employed was $w = 1/[\sigma^2(F) + 0.003F^2]$. The final *R* value was 0.069 (*R'* = 0.073). Calculations were carried out using SHELX 76[18] together with some of our own programs on the Amdahl 5870 computer at the University of Reading. In the final cycles of refinement no shift/error was greater than 0.1σ. In the final Fourier difference maps the maximum and minimum peaks were 0.38 and −0.45 e Å^{-3}. Atomic coordinates are given in Table 1. Torsion angles in the cation are given in Table 2.

Table 1 Atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for $[H_2L^3][PF_6]_2{\cdot}2EtOH$

Atom	*x*	*y*	*z*
Fe(1)	2 578(1)	684(1)	1 107(1)
C(11)	3 831(9)	2 831(8)	1 342(8)
C(12)	2 785(12)	2 717(10)	1 455(10)
C(13)	2 654(10)	2 056(9)	2 541(9)
C(14)	3 625(9)	1 714(9)	3 185(8)
C(15)	4 397(9)	2 246(8)	2 461(8)
C(16)	5 506(8)	2 044(7)	2 790(8)
N(17)	6 806(7)	3 387(7)	3 929(6)
C(18)	6 663(10)	3 433(10)	5 287(9)
C(19)	7 896(12)	4 740(12)	6 487(10)
O(20)	8 918(7)	4 448(6)	6 781(6)
C(21)	9 986(10)	5 550(10)	7 920(10)
C(22)	11 117(10)	5 161(10)	8 403(9)
O(23)	11 562(7)	5 395(6)	7 386(5)
C(24)	12 631(11)	5 176(10)	7 835(10)
C(25)	12 928(9)	5 199(9)	6 597(9)
C(1)	1 025(11)	−518(10)	−702(9)
C(2)	911(12)	−1 238(12)	370(11)
C(3)	2 051(12)	−1 498(10)	995(10)
C(4)	2 641(11)	−970(11)	97(12)
C(5)	2 006(11)	−382(10)	−847(9)
P(1)	4 643(3)	2 494(3)	7 591(2)
F(1)	4 669(6)	1 492(6)	8 720(6)
F(2)	4 759(7)	1 409(7)	6 670(6)
F(3)	4 619(6)	3 534(5)	6 457(5)
F(4)	4 528(7)	3 563(7)	8 518(6)
F(5)	3 167(9)	1 598(9)	6 858(9)
F(6)	6 184(8)	3 412(8)	8 402(8)
O(100)	7 970(12)	1 657(12)	4 264(12)
C(101)	9 300(21)	2 063(16)	4 808(17)
C(102)	9 541(15)	1 258(18)	5 906(17)

Table 2 Torsion angles (°) in the cation of $[H_2L^3][PF_6]_2{\cdot}2EtOH$

(*a*) Ring	
N(17)–C(18)–C(19)–O(20)	−62.9
C(18)–C(19)–O(20)–C(21)	−175.6
C(19)–O(20)–C(21)–C(22)	173.4
O(20)–C(21)–C(22)–O(23)	71.9
C(21)–C(22)–O(23)–C(24)	175.0
C(22)–O(23)–C(24)–C(25)	170.7
O(23)–C(24)–C(25)–N(17*)	60.1
C(24)–C(25)–N(17*)–C(18*)	−173.2
C(25)–N(17*)–C(18*)–C(19*)	55.5
(*b*) Others	
C(13)–C(14)–C(15)–C(16)	−177.3
C(14)–C(15)–C(16)–N(17)	−92.0
C(15)–C(16)–N(17)–C(18)	62.1
C(16)–N(17)–C(18)–C(19)	−179.4

$[L^2{\cdot}NH_4]PF_6$, $C_{45}H_{61}F_6Fe_3N_4O_3P$, $M = 1018.0$, orthorhombic, space group $Cmc2_1$, $a = 19.493(14)$, $b = 11.970(12)$, $c = 19.258(14)$ Å, $U = 4493.5$ Å^3, $D_m = 1.52$ g cm^{-3}, $Z = 4$, $D_c = 1.49$ g cm^{-3}, $\lambda = 0.7107$ Å, $\mu = 10.9$ cm^{-1}, $F(000) = 2120$.

Table 3 Atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for $[L^2 \cdot NH_4]PF_6$

Atom	*x*	*y*	*z*
Fe(1)	5 000	9 451(3)	758(3)
C(60)	5 000	10 042(29)	−199(14)
C(61)	5 587(18)	9 315(26)	−148(18)
C(62)	5 417(15)	8 406(27)	18(26)
C(70)	5 000	7 416(26)	1 860(16)
C(71)	5 000	8 837(29)	1 740(15)
C(72)	5 572(12)	9 542(17)	1 670(10)
C(73)	5 359(11)	10 449(18)	1 563(11)
Fe(2)	7 468(2)	3 284(2)	5 000(2)
C(10)	7 825(13)	3 974(18)	5 915(11)
C(11)	7 243(18)	4 520(31)	5 761(22)
C(12)	6 666(19)	3 758(24)	5 694(18)
C(13)	6 997(15)	2 828(24)	5 914(13)
C(14)	7 734(14)	2 938(21)	6 049(13)
C(15)	8 240(13)	3 122(16)	4 310(11)
C(16)	7 983(12)	2 120(16)	4 419(10)
C(17)	7 142(14)	3 296(21)	3 978(13)
C(18)	7 234(12)	2 253(19)	4 254(11)
C(19)	7 791(18)	3 905(27)	4 115(16)
C(20)	6 438(14)	3 809(21)	3 733(13)
N(21)	5 000	7 225(22)	2 673(14)
C(22)	5 585(11)	7 582(18)	3 008(12)
C(23)	6 279(11)	7 049(16)	2 719(11)
O(24)	6 269(9)	5 949(13)	2 630(8)
C(25)	6 818(16)	5 453(22)	2 674(17)
C(26)	6 851(14)	4 142(19)	2 531(13)
N(27)	6 281(10)	3 640(15)	3 053(9)
C(28)	6 235(9)	2 387(15)	2 870(9)
C(29)	5 557(12)	1 894(18)	3 126(13)
O(30)	5 000	2 420(17)	2 886(11)
N(100)	5 000	4 700(19)	2 487(13)
P	5 000	6 012(10)	5 426(5)
F(11)	5 000	4 952(20)	5 711(23)
F(12)	5 000	7 042(26)	5 053(26)
F(13)	5 540(13)	5 627(22)	4 934(18)
F(14)	4 375(16)	6 312(29)	5 688(28)

Table 4 Torsion angles (°) in the macrocycle $[L^2 \cdot NH_4]PF_6$

C(22*)–N(21)–C(22)–C(23)	171.1
N(21)–C(22)–C(23)–O(24)	−47.3
C(22)–C(23)–O(24)–C(25)	−152.5
C(23)–O(24)–C(25)–C(26)	−176.6
O(24)–C(25)–C(26)–N(27)	−54.2
C(25)–C(26)–N(27)–C(28)	173.5
C(26)–N(27)–C(28)–C(29)	−159.7
N(27)–C(28)–C(29)–O(30)	56.2
C(28)–C(29)–O(30)–C(29*)	178.0

A crystal of approximate size 0.3 × 0.3 × 0.3 mm was set up and data collected as above. 2268 Independent reflections ($0 < h < 21$, $0 < k < 14$, $-22 < l < 22$) were measured of which 1129 with $I > 2\sigma(I)$ were used in subsequent refinement. The iron atom positions were located from the Patterson function and all atoms were located subsequently *via* Fourier methods. All parts of the structure, cation, anion and macrocycle were subject to crystallographic *m* symmetry. The data were of poor quality and so only the iron and phosphorus atoms were refined anisotropically with carbon, nitrogen, oxygen and fluorine atoms treated isotropically. Hydrogen atoms were included in calculated positions with a common refined thermal parameter. An empirical absorption correction was applied. The weighting scheme employed was $w = 1/[\sigma^2(F) + 0.003F^2]$. The final *R* value was 0.086 ($R' = 0.088$). Calculations were carried out as above. In the final cycles of refinement no shift/error was greater than 0.1σ. In the final Fourier difference maps the maximum and minimum peaks were 0.46 and −0.43 e Å^{-3}. Positional parameters are given in Table 3, and ring torsion angles in Table 4.

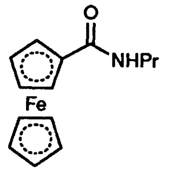
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and bond lengths and angles.

Results and Discussion

Syntheses.—Lehn and co-workers[13,14] first reported the synthesis of triaza-18-crown-6 **1**, and subsequently showed that this macrocycle forms very stable ammonium and primary ammonium complexes by the formation of three complementary NH ··· N hydrogen bonds between host and guest. Following this precedent we decided to incorporate redox-active centres into this type of macrocyclic structural framework.

The condensation of compound **1** with an excess of chlorocarbonylferrocene **2**[15] in the presence of triethylamine and a catalytic quantity of 4-dimethylaminopyridine gave L^1 in yields of up to 85% after purification by column chromatography on alumina (Scheme 1). Since attempts to reduce the amide linkages using diborane, lithium aluminium hydride or diisobutylaluminium hydride failed, a new synthetic pathway was devised to synthesise L^2. Refluxing a mixture of 3 mol of trimethylammoniomethylferrocene iodide **3**,[16] **1** and anhydrous potassium carbonate in acetonitrile solution followed by column chromatography gave L^2 in 86% yield (Scheme 2). The analogous reaction of 2 mol of **3** and diaza-18-crown-6 **4** gave L^3 in 70% yield (Scheme 3).

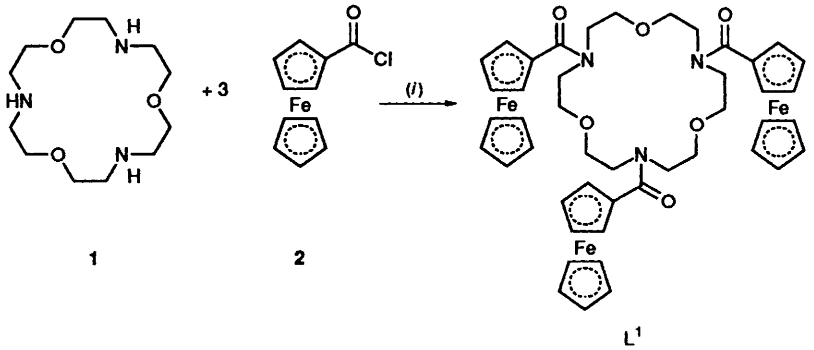
The new primary amine-functionalised aza crown ethers **5** and **6** were prepared by reaction of the appropriate aza crown ether with acrylonitrile followed by diborane reduction. Condensation of **5** and **6** with an excess of chlorocarbonylferrocene **2** in the presence of triethylamine followed by column chromatography gave L^4 and L^5 in yields of 69 and 65% respectively (Scheme 4). Reaction of **6** with 4 mol of **3** in an acetonitrile solution containing potassium carbonate gave L^6 in 92% yield. The multiple quinone-containing macrocyclic ligand L^7 was prepared in 55% yield by the reaction of 3 mol of 2-bromomethylanthraquinone **7**[17] with **1** in the presence of potassium carbonate (Scheme 5). The mixed ferrocene-quinone ligand L^8 was synthesised *via* compounds **8**,[14] **9** and **10** (Scheme 6) and subsequently alkylated with 1 equivalent of **7**. The model compound **11** was prepared by reaction of **2** with diisopropylamine.



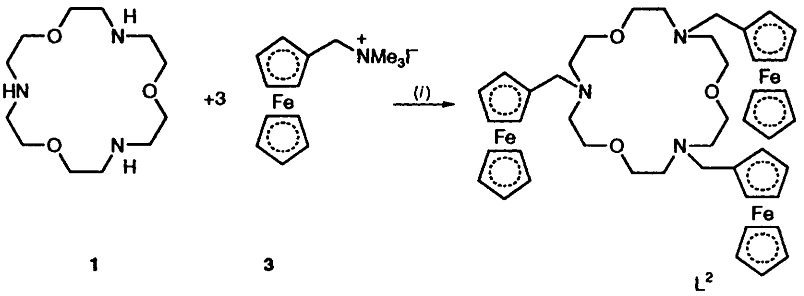
11

The structures of all these new ligands were characterised on the basis of spectroscopic and analytical evidence (see Experimental section). The elemental analyses generally showed good agreement between the values expected and those obtained, however small discrepancies found for some compounds were attributed to their ability to include solvent molecules, which proved difficult to remove even under vacuum.

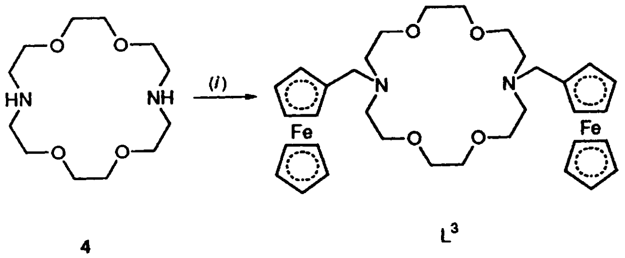
X-Ray Structural Investigation of $[H_2L^3][PF_6]_2 \cdot 2EtOH$.—Orange crystals of the hydrogen hexafluorophosphate salt of L^3 suitable for X-ray structural investigations were obtained from an ethanol–acetone solvent mixture. The structure contains discrete centrosymmetric cations (Fig. 1), PF_6^- anions and solvent ethanol molecules. The centrosymmetric cations contain a 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane moiety



Scheme 1 (*i*) NEt_3, 4-dimethylaminopyridine



Scheme 2 (*i*) K_2CO_3



Scheme 3 (*i*) Compound 3 (2 mol), K_2CO_3

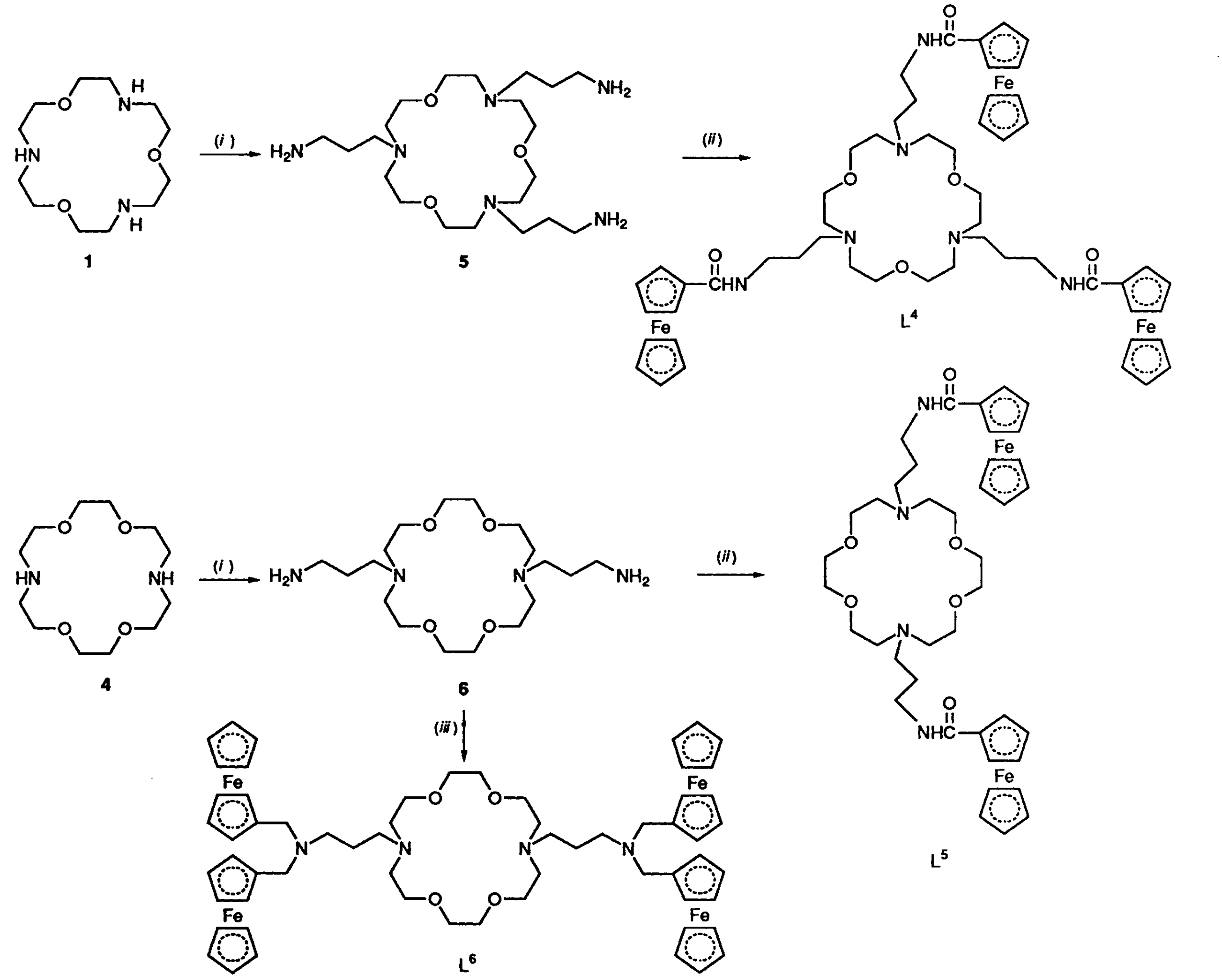
with ferrocenylmethyl substituents on the two nitrogen atoms. The two cyclopentadienyl rings are eclipsed. The conformation of the 18-membered ring is described by the torsion angles in Table 2. All bar two of the C–X–C–C (X = O or N) torsion angles are *trans* with angles within 10° of 180°. It may be significant that the exceptions, C(25)–N(17*)–C(18*)–C(19*) (* = symmetry operation $2 - x$, $1 - y$, $1 - z$) and the symmetry related angle C(25*)–N(17)–C(18)–C(19) involve the nitrogen atoms connected to the ferrocenylmethyl groups. A contributing factor could also be the formation of hydrogen bonds to the solvent molecules. The X–C–C–X torsion angles are all *gauche* with a +,−,−,+,+,− pattern. This contrasts with the familiar D_{3d} conformation of 18-crown-6 rings which has the *gauche* pattern +,−,+,−,+,−. The present pattern represents an unusual conformation of the 18-membered ring not usually found in 18-crown-6 structures.[19,20] The O–C–C–O torsion angle at 71.9 is significantly larger than the O–C–C–N torsion angles (−62.9, 60.1°), presumably a consequence of the shorter C–O bond lengths.

The two solvent ethanol molecules are found above and below the cavity, forming hydrogen bonds to the NH groups in the ring [O(100)···N(17) 2.71 Å]. There are no other close contacts in the structure less than the sum of van der Waals radii.

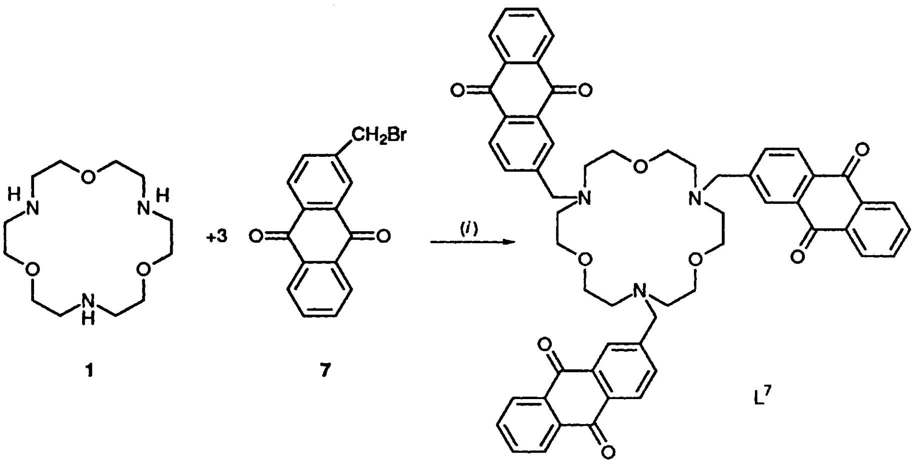
Co-ordination Studies.—Solution complexation studies with the ammonium cation were investigated using ^{13}C and ^1H NMR spectroscopy.[21,22] In a typical titration experiment the stepwise addition of a concentrated solution of ammonium thiocyanate, in 0.5 equivalent increments, in deuteriated acetonitrile to a dilute deuteriated acetonitrile solution of L^4 resulted in downfield shifts of the OCH_2 and cyclopentadienyl carbons of up to 1.5 ppm. Interestingly a downfield shift of 0.5 ppm was also observed for the carbonyl amide carbon of L^4 suggesting an electrostatic interaction with the NH_4^+ guest. No further significant shifts were seen after addition of 1 equivalent of ammonium thiocyanate, suggesting a solution stoichiometry of 1:1. The results of analogous experiments with L^2 (see Fig. 2), L^3 and L^5–L^8 also suggested 1:1 solution complexes with NH_4^+. However, with L^1 very small shifts ($\leqslant$0.04 ppm) in the ^{13}C NMR spectra were observed indicating very weak complexation with the ammonium cation.

Attempts were made at isolating ammonium complexes of L^2–L^8 by refluxing acetonitrile solutions of the respective ligand with an excess of ammonium hexafluorophosphate or thiocyanate. With L^3–L^8, upon cooling oily products were always obtained which despite repeated attempts at purification by Sephadex column chromatography failed to crystallise. As a consequence, although fast atom bombardment mass spectrometry detected the respective $[L + NH_4]^+$ cation, satisfactory elemental analyses of the desired complexes were not obtained. However with L^2 an ammonium complex was prepared and crystals of X-ray quality isolated.

X-Ray Structural Investigation of $[L^2{\cdot}NH_4]PF_6$.—Orange crystals of the ammonium complex of L^2 suitable for X-ray structural investigations were grown from acetonitrile solvent. The structure consists of discrete NH_4^+ cations, PF_6^-, and neutral macrocycle molecules, all with crystallographically imposed C_m symmetry. In the macrocycle the mirror plane passes through an oxygen atom and nitrogen atom in the 18-membered ring and also the ferrocenylmethyl moiety attached to the nitrogen atom. The cation is positioned on this mirror plane within the cavity of the macrocycle as shown in Fig. 3 which also includes the numbering scheme. The ammonium cation forms close contacts with all six potential hydrogen-bond acceptors in the 18-membered ring. Distances are O(24) 2.90, N(27) 3.01, O(30) 2.84 and N(21) 3.04 Å. We were not able to locate the hydrogen atoms so it would seem likely that the hydrogen bonds are disordered over these six short distances. The macrocycle has a unique conformation in that of the three



Scheme 4 (*i*) Acrylonitrile, B_2H_6; (*ii*) compound **2**, NEt_3; (*iii*) compound **3** (4 mol), K_2CO_3



Scheme 5 (*i*) K_2CO_3

ferrocenylmethyl linkages two are on one side of the ring and one on the other (Fig. 4). The Fe–C distances are all within the expected range 1.98(3)–2.08(3) Å. The two C_5H_5 rings in the unique $Fe(C_5H_5)_2$ moiety are staggered astride the mirror plane while those in the others are more eclipsed. The conformation of the triaza-18-crown-6 ring is described by the torsion angles in Table 4. This is a somewhat unusual conformation in that while the X–C–C–X angles (X = O or N) are all *gauche* and the C–C–X–C angles are all *trans*, the signs of the X–C–C–X angles follow the order −,−,+,−,+,+, rather than the −,+,−,+,−,+ order in the well known D_{3d} conformation of 18-crown-6.

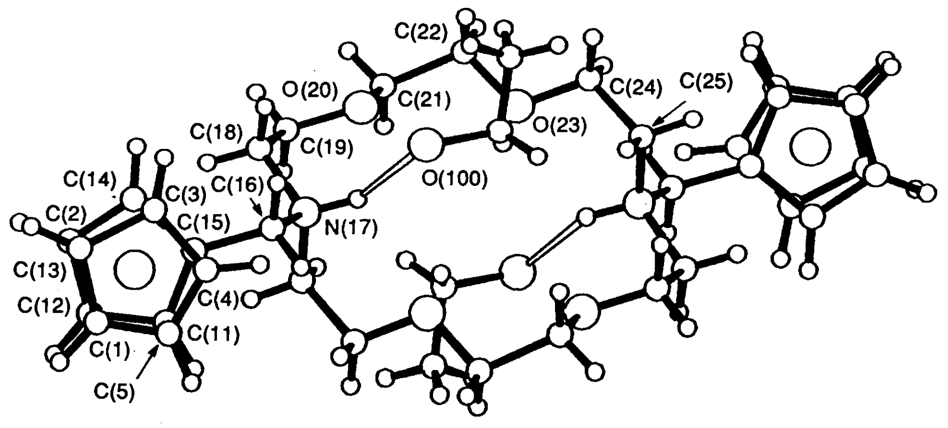


Fig. 1 Structure of $[H_2L^3][PF_6]_2 \cdot 2EtOH$. The open bond represents a hydrogen bond between the protonated nitrogen and the ethanol solvent

Table 5 Electrochemical data for L^1–L^6 and compound **11**

	L^1	L^2	L^3	L^4	L^5	L^6	**11**
$E_f{}^a$/V	$+0.67^b$	$+0.43^b$	$+0.41^c$	$+0.62^b$	$+0.54^c$	$+0.44^d$	+0.59
$\Delta E_p{}^e$/mV	80	90	90	100	100	90	80
$\Delta E(NH_4{}^+)^f$/mV	< 10	210^g	60	70^h	150^h	< 10	< 10
$\Delta E(K^+)^f$/mV	< 10	40	60	50	85	< 10	< 10
$\Delta E(NMeH_3{}^+)^f$/mV	< 10	—	—	< 10	< 10	—	< 10
$\Delta E[N(CH_2CH_2Ph)H_3{}^+]^f$/mV	< 10	—	—	< 10	< 10	—	< 10

[a] Solutions were *ca.* 2 × 10^{-3} mol dm^{-3} in compound and potentials were determined with reference to the saturated calomel electrode. [b] Three-electron reversible oxidation process. [c] Two-electron reversible oxidation process. [d] Four-electron reversible oxidation process. [e] Separation between anodic and cathodic peak potentials; values for ferrocene under identical conditions ranged from 80 to 90 mV. [f] Shift in respective ferrocenyl oxidation potential produced by the presence of guest cations (2 equivalents) added as their thiocyanate salts for potassium and ammonium, and their picrate salts for methyl- and phenethyl-ammonium. [g] Evolution of new redox wave. [h] E_{pa} only seen, no E_{pc} of complex observed.

Table 6 Electrochemical data (E_f/V)[a] for L^7 and L^8

L^7	L^8
-0.43^b	-0.44^b
-0.69^c	-0.70^c
	$+0.42^d$

[a] Solutions were *ca.* 2 × 10^{-3} mol dm^{-3} in compound and potentials were determined with reference to the saturated calomel electrode. [b] Reversible reduction wave. [c] Quasi-reversible reduction wave. [d] Reversible ferrocenyl oxidation wave.

Electrochemical Studies.—The electrochemical properties of L^1–L^6 and 'model' compound **11** were investigated in acetonitrile using cyclic voltammetry with $NBu^n{}_4BF_4$ as the supporting electrolyte. Each compound exhibited a one-wave reversible redox oxidation in the 0.4–0.7 V region (*versus* SCE) typical of a substituted ferrocene derivative (Table 5). With L^1–L^6 the electrochemical findings suggest the two, three or four ferrocene moieties present in these receptors become oxidised in one step. Differential-pulse voltammetric experiments also revealed only one oxidation wave for each ligand. Coulometric studies confirmed the respective oxidation waves of L^1–L^6 to be multielectron processes.

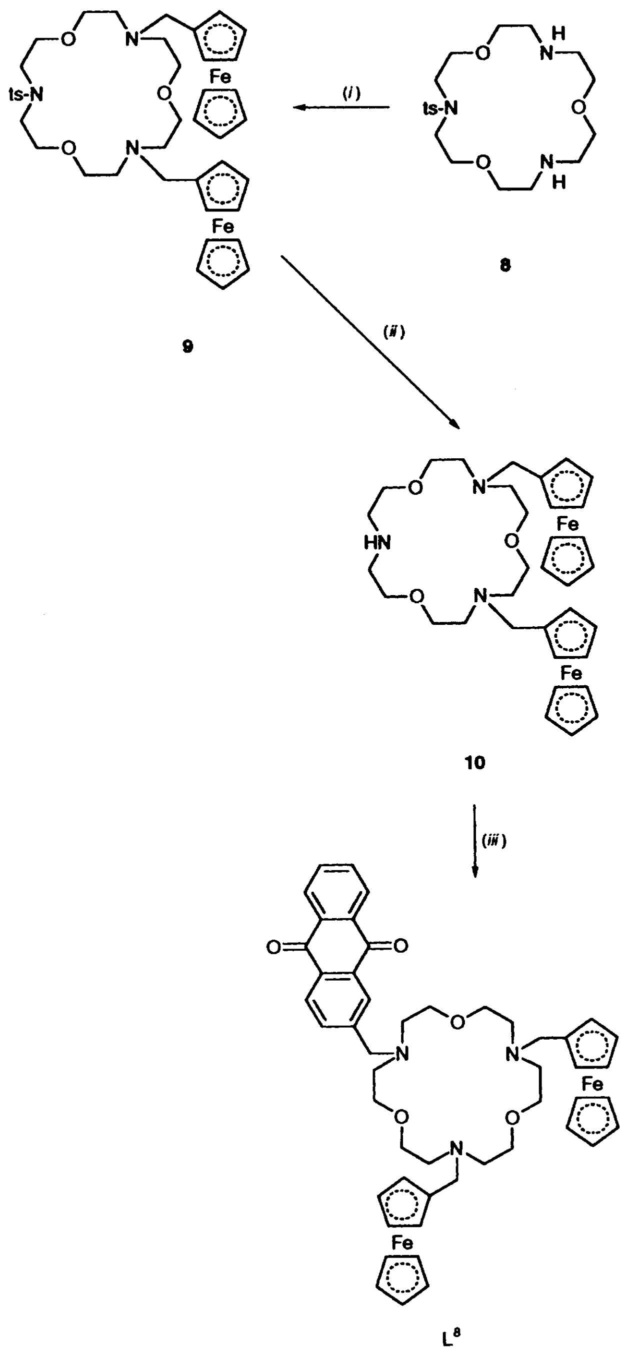
Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of $NH_4{}^+$ and K^+ cations to the electrochemical solutions of L^1–L^6, **11** and the results are summarised in Table 5. Significant anodic perturbations were observed with the two cationic guests only in the case of L^2–L^5. Comparing the electrochemical recognition results of the methylene-linked ferrocenyl ligands L^2 and L^3 it is noteworthy that the respective magnitudes of $NH_4{}^+$ and K^+ cationic guest perturbations are approximately the same for L^3, however with L^2 a significant difference is observed. At substoichiometric equivalents of $NH_4{}^+$ and L^2 the evolution of a new redox wave corresponding to the ammonium complex is observed at a more anodic potential (ΔE = 210 mV) than that of the free ligand (Fig. 5). Gokel and co-workers[23] have concluded from their recent electrochemical metal-cation recognition studies of quinone and nitroaromatic crown ether redox-active systems that two distinct cyclic voltammetric (CV) waves will be observed only when the neutral ligand–guest Group IA metal cation binding constant is large and an anodically shifted single CV wave will result from weaker guest metal cation–ligand interactions. Clearly L^2 is exhibiting a degree of selectivity for $NH_4{}^+$ over K^+. To test this hypothesis further, electrochemical competition recognition studies[24] were undertaken. When an equimolar acetonitrile mixture of $NH_4{}^+/K^+$ was added to an electrochemical solution of L^2 the appearance of a new anodically shifted CV wave at a similar potential to that previously found with the $NH_4{}^+$ guest cation alone was observed. These competition results suggest L^2 to be a first-generation prototype amperometric sensor for $NH_4{}^+$ over the K^+ cation.

Ligands L^4 and L^5 both exhibit single CV wave anodic perturbations in the presence of K^+, however with $NH_4{}^+$ the evolution of a new anodically shifted oxidation wave *only* was observed (Fig. 6). No corresponding reduction wave of presumably the respective ammonium–ligand complex was in either case detectable. In these two ligand systems the primary interaction between the ammonium guest and ferrocene redox-active centre of the respective host probably results from the additional co-ordination of the aza crown ether-complexed $NH_4{}^+$ to the respective amide carbonyl oxygen donor in a lariat-type fashion[25] *via* hydrogen bonding (Fig. 7). Evidence for this type of interaction comes from the significant downfield shifts of the respective amide carbonyl carbons observed in ^{13}C NMR titration experiments of L^4 and L^5 with NH_4SCN. This host amide carbonyl oxygen–ammonium cation hydrogen-bonding interaction may be switched off when the respective ferrocene redox centres of L^4 and L^5 are oxidised. The proximal mutual electrostatic repulsion between ferrocenium and the positively charged guest is enough to cancel the hydrogen-bonding interaction and so communication between redox centre and guest cation is broken. This type of electrochemical behaviour is analogous to that reported by Hall *et al.*[9] on their ferrocene cryptands complexing lanthanide guest cations.

Further support for the importance of this lariat-type amide carbonyl oxygen–NH_4^+ hydrogen-bonding interaction can be gained from electrochemical experiments involving the addition of methyl- and phenethyl-ammonium picrate salts to the respective electrochemical solutions of L^4 and L^5. Insignificant anodic shifts (< 10 mV) of the respective ferrocenyl oxidation wave of L^4 and L^5 were observed for both $R\text{-}NH_3^+$ guest cations implying that the methyl and phenyl groups are sterically preventing lariat-type co-ordination.

Also of note are the very small anodic shifts observed on addition of K^+ or NH_4^+ to electrochemical solutions of L^6. The structure of L^6 is similar to that of L^5 which displays large anodic perturbations (Table 5) except that L^6 contains no amide carbonyl groups. Thus the ferrocenecarboxamido–cationic guest through-bond electrostatic interaction is a crucial component for electrochemical recognition of NH_4^+ and K^+ cations in these types of redox-active host systems. Indeed we[11] and Hall *et al.*[9] have recently described simple ferrocene amide compounds which electrochemically respond to Li^+ and a range of divalent metal cations *via* amide carbonyl co-ordination.

The results of electrochemical investigations of L^7 and L^8 are reported in Table 6. With both ligands, at cathodic potentials, two reduction waves were observed, the first reversible wave corresponding to the formation of the anthraquinone anion radical. In the case of L^8 an additional reversible ferrocene redox couple was seen at anodic potentials. Surprisingly very small anodic shifts ($\leqslant 10$ mV) of the respective quinone redox centres were noticed on addition of NH_4^+ and K^+ to



Scheme 6 (*i*) Compound **3** (2 mol), K_2CO_3; (*ii*) $LiAlH_4$; (*iii*) compound **7**

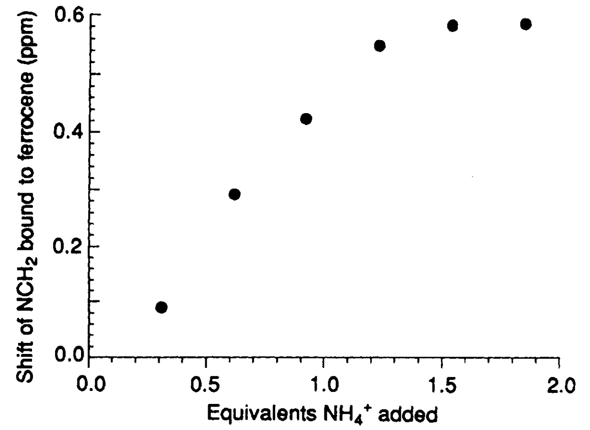


Fig. 2 Proton NMR titration of L^2 and NH_4^+ in CD_3CN

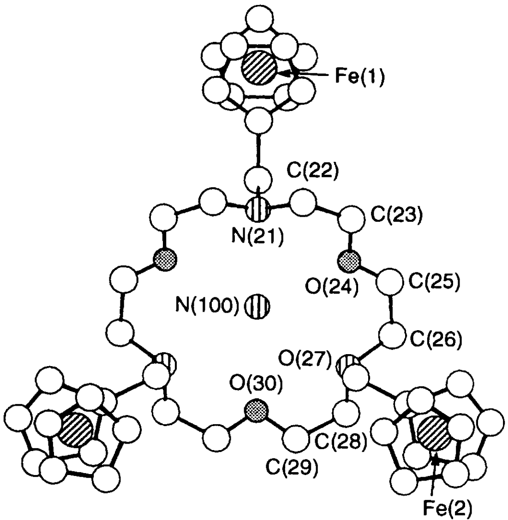


Fig. 3 Structure of $[L^2{\cdot}NH_4]PF_6$

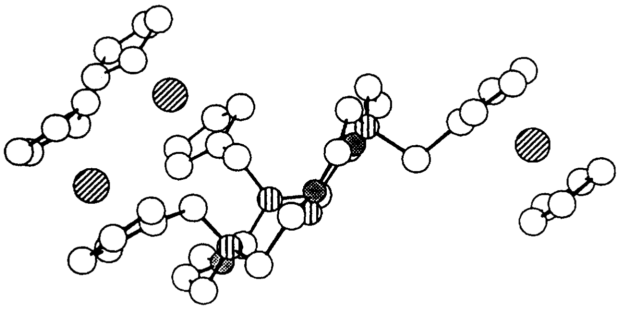


Fig. 4 Structure of $[L^2{\cdot}NH_4]PF_6$ illustrating the respective positions of the appended ferrocene moieties

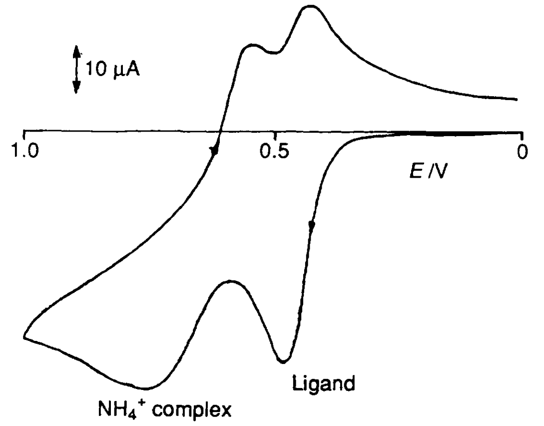


Fig. 5 Cyclic voltammogram of L^2 +0.5 equivalent of NH_4SCN

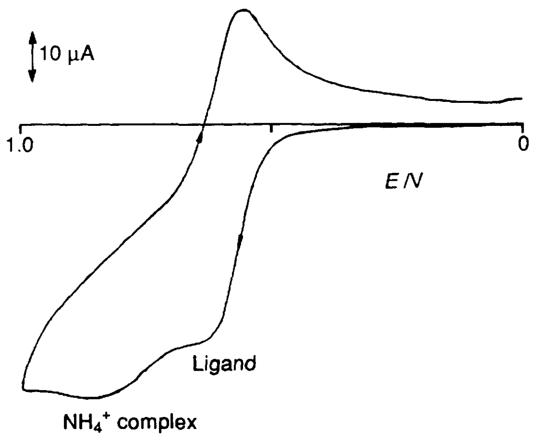


Fig. 6 Cyclic voltammogram of L^5 +0.5 equivalent of NH_4SCN

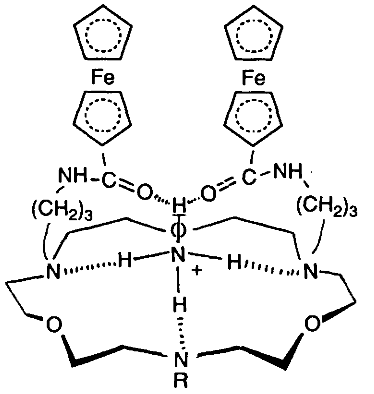


Fig. 7 Proposed 'lariat' co-ordination of NH_4^+ with L^4

electrochemical solutions of L^7 and L^8. Gokel and co-workers[25,26] have shown from their work on quinone-appended crown ethers that the magnitude of the anodic shift is dependent on ion pairing between the guest cation and the reduced anthraquinone anion radical, and the extra stabilisation by the crown ether binding site in close proximity to the quinone moiety. For both ligands the lack of electrochemical recognition suggests that either the crown ether-bound cation is too far away from the quinone redox centre to influence its electron density by ion pairing, or for steric reasons electrostatic communication is negated.

An ammonium cation-induced one-wave anodic shift of 50 mV of the ferrocene–ferrocenium redox couple was observed however for L^8 of comparable magnitude to that found with L^2 and L^3 (Table 1).

Conclusion

A series of new redox-active di- and tri-aza crown ether macrocyclic ligands containing multiple ferrocene and quinone moieties have been prepared, including the first reported mixed ferrocene–quinone macrocyclic ligand L^8. Co-ordination chemical studies revealed L^2–L^8 to form solution 1 : 1 complexes with the NH_4^+ guest cation and with L^2 an ammonium complex was isolated and its structure determined. The ferrocene-appended ligands L^2–L^5 and L^8 electrochemically recognise NH_4^+ and K^+ guest cations. The largest magnitude of anodic shift of the respective ferrocene–ferrocenium redox couples was exhibited by L^2 (210 mV) with the evolution of a new CV wave corresponding to the ammonium complex. Electrochemical recognition competition experiments with NH_4^+ and K^+ showed L^2 to be a first-generation prototype amperometric sensor for NH_4^+. Ligands L^4 and L^5 both containing secondary amide groups linking the ferrocene redox centres to the aza crown ether macrocycles electrochemically sense the NH_4^+ guest cation primarily *via* host ferrocenecarboxamide oxygen–NH_4^+ hydrogen-bonding electrostatic interactions. Cyclic voltammetric experiments suggest this through-bond electrostatic communication is negated when the respective ferrocene redox centres are oxidised, presumably as a result of proximal mutual electrostatic charge repulsion between ferrocenium and cationic ammonium guest.

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