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Towards conformationally dependent redox-responsive molecular switches. New polyferrocene bis benzo crown ether receptors

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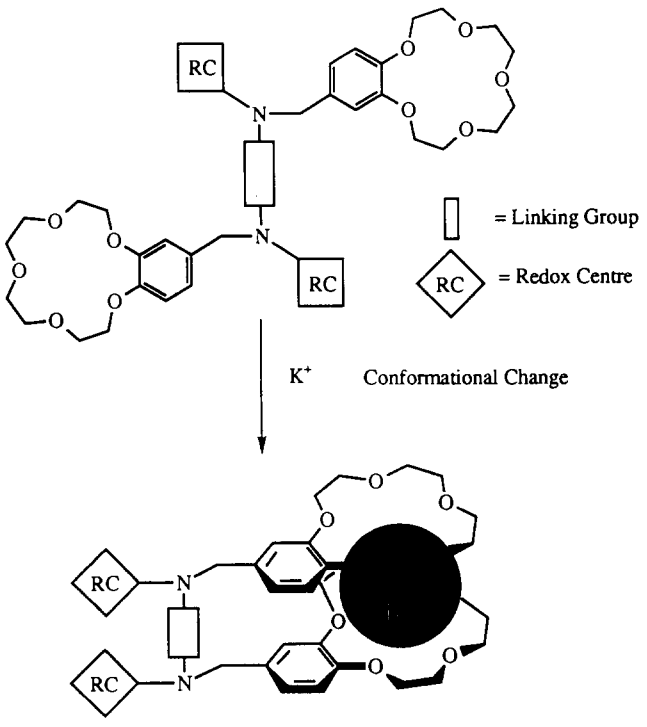
Abstract

New polyferrocene bis benzo-15-crown-5 ligands have been prepared and shown to form 1:1 intramolecular sandwich complexes with the potassium cation. Electrochemical investigations reveal that both receptors undergo small anodic perturbations of the respective ferrocene–ferrocenium redox couples in the presence of alkali metal cations.

Keywords: Iron; Polyferrocene; Crown ethers; Molecular switches; Redox couples; Potassium complexes

1. Introduction

The synthesis of redox-active crown ether ionophores capable of electrochemically recognising Group 1 and 2 metal cations either through space and/or via various conjugated bond linkages is well established [1–3]. A new approach to the development of amperometric-sensing devices of the future may centre on using bound guest induced conformational changes of a redox-active ligand to produce a modification of the electronic environment of the redox centre, and hence to perturb its redox-responsive behaviour. With this goal in mind, we have synthesized a new polyferrocene bis benzo 15-crown-5 ether receptor molecule designed to undergo a conformational change upon formation of an intramolecular potassium cation sandwich complex, bringing the respective redox centres in close proximity to one another and consequently altering their redox properties (Scheme 1).



Scheme 1.

2. Results and discussion

2.1. Syntheses

The condensation of two equivalents of 4-formyl benzo-15-crown-5 (**1**) [4] and the appropriate diamine, ethylene diamine (**2**) or diethylene triamine (**3**), in a melt reaction gave the respective Schiff base products (**4**) and (**5**) as pale yellow solids in 40% yields (Scheme 2) [5].

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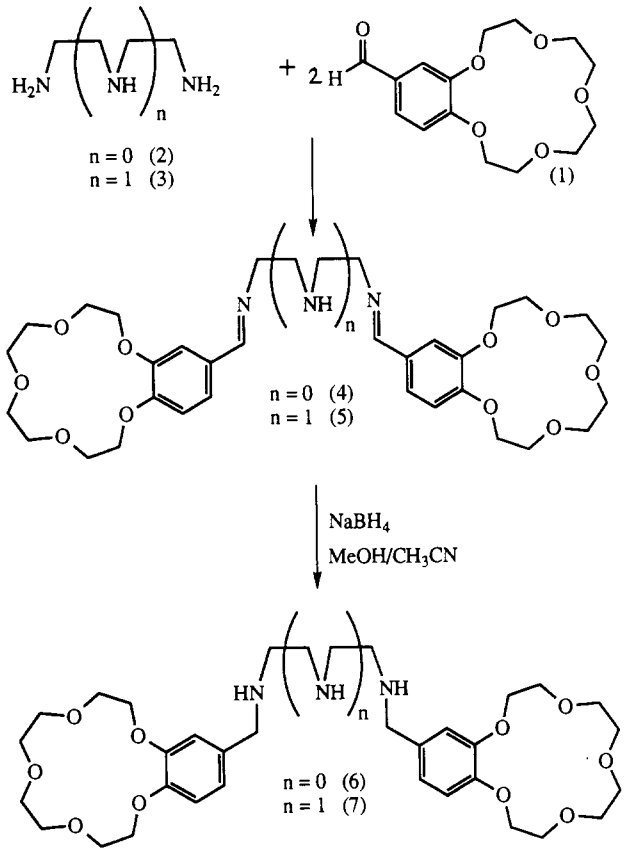
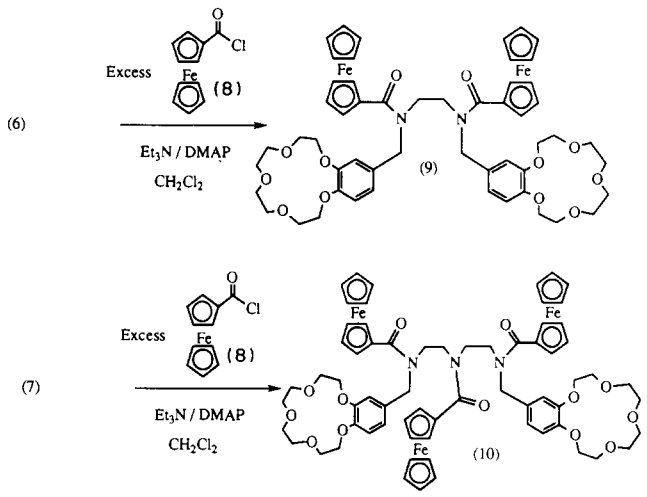


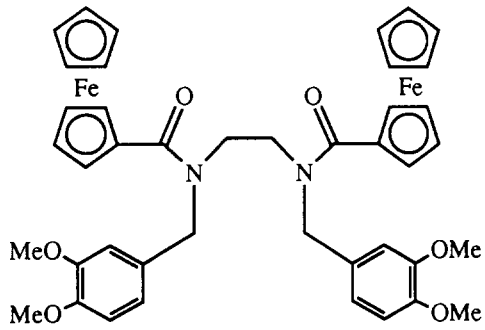
Scheme 2.

The imine bonds were reduced with sodium borohydride in methanol to give the secondary amine bis benzo crown ethers (**6**) and (**7**) as colourless oils in 52% and 59% yields respectively (Scheme 2). The condensation of (**6**) and (**7**) with an excess of chlorocarbonyl ferrocene (**8**) [6] in dry dichloromethane in the presence of triethylamine and DMAP (dimethylamine pyridine) gave, after alumina column chromatography, the new redox active ionophores (**9**) and (**10**) as orange solids in low yields (Scheme 3). Analogous synthetic

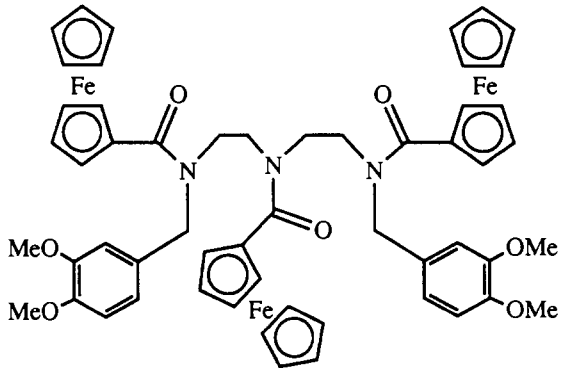


Scheme 3.

procedures were used to prepare the model veratrole analogues (**11**) and (**12**). All these new compounds gave spectroscopic and analytical data in accord with assigned structures (see Experimental details).



(11)



(12)

Table 1
Electrochemical data [a]

Compound	(9)	(10)
E_{pa}(V)	0.62	0.62
E_{pc}(V)	0.53	0.52
$\Delta E(K^+)$mV [b]	10	10
$\Delta E(Na^+)$mV [b]	< 10	< 10
$\Delta E(Li^+)$mV [b]	< 10	< 10

[a] Obtained in acetonitrile containing 0.2 mol dm^{-3} $Bu_4N^nBF_4$ as supporting electrolyte. Solutions were ca. 2×10^{-3} mol dm^{-3} in compound, and potentials were determined with reference to a standard calomel electrode (S.C.E.).

[b] One wave anodic shift in oxidation potential produced by the presence of four equivalents of metal cations added as KPF_6, $NaPF_6$ or $LiBF_4$ salts.

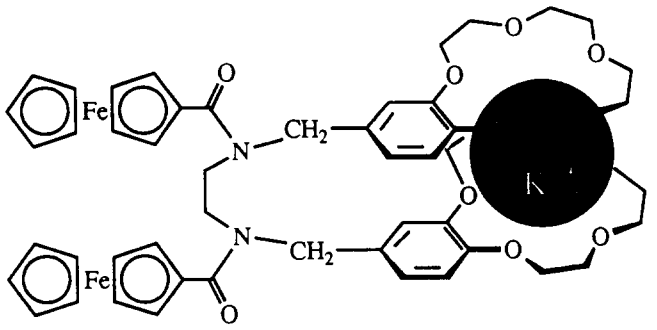


Fig. 1.

3. Coordination studies

Proton NMR titration of (**9**) and (**10**) with KPF_6 in acetonitrile revealed both compounds form in solution 1:1 intramolecular sandwich complexes with the potassium cation. A number of alkyl, vinyl and azo linked bis benzo 15-crown-5 ligands are well-known to exhibit this mode of K^+ coordination [7]. In the case of (**9**) a solid-state potassium complex was isolated whose elemental analysis and fast atom bombardment mass spectrum (**9**). $K^+ = 1083$ complex ion) was in agreement with 1:1 stoichiometry (Fig. 1.). No ^1H NMR evidence of K^+ complexation by the veratrole model analogues (**11**), (**12**) was observed.

4. Electrochemical studies

The electrochemical properties of all these polyferrocene compounds were investigated in acetonitrile by cyclic voltammetry with Bu_4NBF_4 as the supporting electrolyte. Each compound exhibited a single reversible oxidation wave, suggesting that the respective ferrocenoyl redox centres act independently (Table 1). Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of K^+, Na^+ and Li^+ cations to the electrochemical solutions, and the results are also summarised in Table 1. Disappointingly in the case of all the metal cations, only relatively small anodic perturbations of the respective ferrocene–ferrocenium redox couples of (**9**) and (**10**) were observed. This suggests that the binding of potassium cations, although resulting in a dramatic conformational change with formation of an intramolecular sandwich complex, as evidenced by NMR spectroscopy and FAB-MS, does not significantly affect the electronic environments of the respective ferrocene redox centres.

5. Conclusions

New polyferrocene bis benzo 15-crown-5 ligands (**9**) and (**10**) were designed in each case to form a 1:1 intramolecular sandwich complex with a potassium cation, and as a consequence of this metal cation induced conformational change, alter the electronic, and hence redox properties of the ferrocene moieties.

Although spectroscopic and analytical evidence suggested that 1:1 potassium complexes were indeed produced with these ligands, the electrochemical investigations proved disappointing, only small anodic perturbations of the respective ferrocene–ferrocenium redox couples were observed on addition of K^+, and also Na^+ and Li^+ cations.

6. Experimental details

6.1. Solvent and reagent pre-treatment

Where necessary, solvents were purified prior to use and stored under nitrogen. Acetonitrile was dried over class 4 Å molecular sieves (4–8 mesh), and then distilled from CaH_2. Diethyl ether was dried over sodium wire and distilled from sodium immediately prior to use. Dimethyl formamide (DMF) was dried overnight over activated class 3 Å molecular sieves. Ethanol was distilled under nitrogen from sodium ethoxide. Methanol was distilled from $CaSO_4$ and stored over class 4 Å molecular sieves. Tetrahydrofuran (THF) and toluene were distilled from sodium with benzophenone as an indicator. Triethylamine and dichloromethane were distilled from CaH_2. Unless otherwise stated, commercial grade chemicals were used without further purification. The following compounds were prepared by published procedures: 4-formyl-benzo-15-crown-5 [4] and chlorocarbonylferrocene [6].

6.2. Instrumentation

NMR spectra were recorded on a Bruker AM 300 instrument, operating at 300 MHz for ^1H NMR and 75.42 MHz for ^{13}C NMR spectra. Infrared spectra were recorded on a Mattson 10410E "Polaris" Fourier transform spectrometer. Electrochemical measurements were conducted with a Princeton Applied Research Potentiostat/Galvanostat Model 273. Melting points were recorded on a Gallenkamp melting point apparatus. Fast atom bombardment mass spectra (FAB-MS) were carried out at University College, Swansea. All elemental analyses were carried out by the Inorganic Chemistry Laboratory Microanalysis Service.

6.3. Syntheses

6.3.1. N,N'-Bis[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin-16-yl)methylidene]ethylenediamine (4) was prepared using a modified procedure of Lockhart and co-workers [8]

4-Formylbenzo-15-crown-5 (**1**) (2.0 g, 14.4 mmol) was stirred in a flask maintained at 120°C. Ethylene diamine (**2**) (0.436 g, 7.2 mmol) was added dropwise, and the mixture was heated for 30 min then was allowed to cool. The product was triturated with diethyl ether to give a pale yellow solid, 1.72 g, 38%.

^{1}H NMR ($CDCl_3$) δ: 3.76 (16H, s, OCH_2CH_2O), 3.91 (12H, m, Ar–OCH_2CH_2O– and NCH_2), 4.16 (8H, m, Ar–OCH_2–), 6.62 (2H, d, $J = 9.0$ Hz, Ar–H), 7.10 (2H, d, $J = 9.0$ Hz, Ar–H), 7.35 (2H, s, Ar–H), 8.14 (2H, s, N=CH). ^{13}C NMR ($CDCl_3$) δ: 61.42 (NCH_2), 68.71, 69.20, 70.43 and 71.01 (OCH_2), 111.24, 112.57, 123.10, 129.61, 149.12 and 151.26 (Ar), 162.00 (C=N).

Melting point: 109–110°C. IR: 1652 cm^{-1}, –C=N– stretch. Anal. Calc. for $C_{34}H_{44}N_2O_{10}$: C; 62.3; H, 7.2;N, 4.5%. Found: C, 62.0; H, 7.3; N, 5.0%. EIMS M^+ @616.

6.3.2. N,N'-Bis[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin · 16-yl)methylidene]diethylenetriamine (5)

Compound (**5**) was prepared by the procedure described for (**4**) starting from (**1**) (0.5 g, 3.6 mmol) and diethylene triamine (0.19 g, 1.81 mmol), the yield was 0.25 g, 21%.

^{1}H NMR ($CDCl_3$) δ: 2.95 (4H, s, br, NCH_2), 3.73 (20H, m, OCH_2CH_2O and $=NCH_2$), 3.85 (8H, m, Ar–OCH_2CH_2–), 4.15 (8H, m, Ar–OCH_2CH_2–), 6.78 (2H, d, $J = 9.0$ Hz, Ar–H), 7.05 (2H, d, $J = 9.0$ Hz, Ar–H), 7.30 (2H, s, Ar–H), 8.14 (2H, s, N=CH). Anal. Calc. for $C_{34}H_{49}N_3O_{10}$: C, 61.9; H, 7.5; N, 6.4.% Found: C, 60.8; H, 7.6; N, 6.2%. Melting point: 92–94°C. IR: 1653 cm^{-1}, –C=N–stretch.

6.3.3. N,N'-Bis[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin-16-yl)methyl]ethylenediamine (6)

To a solution of (**4**) (0.50 g, 0.8 mmol) in dry acetonitrile (36 ml) was added sodium borohydride (0.61 g, 16 mmol). The mixture was refluxed overnight, then cooled, and water (20 ml) was added. The solvent was removed in vacuo, and the residue redissolved in $CHCl_3$ (70 ml) and the solution was washed with water (3 × 100 ml) then reduced in vacuo to 10 ml. Hydrochloric acid (70 ml, 10%) was added and the aqueous layer was separated and washed with $CHCl_3$ (3 × 50 ml). Saturated LiOH solution was added to the aqueous layer to give pH 14, and the amine was extracted into CH_2Cl_2 (4 × 100 ml). The CH_2Cl_2 layer was then washed with water (2 × 100 ml), and dried over $MgSO_4$, filtered, and reduced in vacuo to give the product as a yellow oil, 0.26 g, 52%.

^{1}H NMR ($CDCl_3$) δ: 2.75 (4H, s, NCH_2CH_2N), 3.70 (20H, m, OCH_2CH_2O and Ar–CH_2N), 3.82 (8H, m, Ar–OCH_2CH_2O), 4.10 (8H, m, Ar–OCH_2CH_2O), 6.75 and 6.85 (6H, m, Ar–H).

An analytical sample of the hydrochloride salt of (**6**) was made by washing a dichloromethane solution of (**6**) with 10% $HCl_{(aq)}$ and then separating the aqueous layer and removing the water in vacuo. Ethanol was then added and removed in vacuo to give (**6**). 2 HCl as a white powder in quantitative yield.

^{1}H NMR (D_2O) δ: 3.48 (4H, s, NCH_2CH_2N), 3.72 and 3.79 (16H, d, OCH_2CH_2O), 3.94 (8H, s, $ArOCH_2CH_2O$), 4.21 (8H, s, $ArOCH_2$), 4.26 (4H, s, NCH_2Ar), 7.10 and 7.14 (6H, d, Ar–H). ^{13}C NMR (D_2O) δ: 43.34 (NCH_2CH_2N), 52.19 (NCH_2Ar), 68.83, 69.42, 70.10 and 70.56 (OCH_2), 114.29, 115.39, 124.17, 124.30, 148.88 and 149.70 (Ar). Anal. Calc. for $C_{32}H_{48}N_2O_{10}$. 2HCl.H_2O: C, 54.0; H, 7.4; N, 3.9%. Found: C, 54.5; H, 7.0; N, 3.8%. Melting Point 107–108.5°C. IR: 2750 cm^{-1} NH^+ stretch. FAB-MS (**6**).H^+@621.

6.3.4. N,N'-Bis[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin-16-yl)methyl]diethylene triamine (7)

Compound (**7**) was prepared by the procedure described for (**6**) but starting from (**5**) (0.25 g, 3.8 mmol), $NaBH_4$ (0.30 g, 8 mmol) and CH_3CN (20 ml). The yield was 0.15 g, 59%.

^{1}H NMR ($CDCl_3$) δ: 2.73 (8H, m, Ar–OCH_2CH_2), 3.70 (22H, m, OCH_2CH_2O, NH and N–CH_2–Ar), 3.90 (8H, m, Ar–OCH_2CH_2), 4.17 (8H, m, Ar–OCH_2), 6.83(4H, br, Ar–H), 6.90 (2H, s, br, Ar–*H*).

An analytical sample of the hydrochloride salt (**7**).3HCl was produced in an analogous manner.

^{1}H NMR (D_2O) δ: 3.47 (8H, s, NCH_2CH_2N), 3.72 and 3.77 (16H, m, OCH_2CH_2O), 3.94 (8H s, $ArOCH_2CH_2O$), 4.21 (8H, s, $ArOCH_2$), 4.27 (4H, s, NCH_2Ar), 7.08 and 7.13 (6H, d, ArH). ^{13}C NMR (D_2O) δ: 43.63 and 44.61 (NCH_2CH_2N), 52.31 (NCH_2Ar), 69.03, 69.61, 70.22 and 70.75 (OCH_2), 114.38, 115.59, 123.98, 124.50, 149.04 and 149.95 (Ar). Anal. Calc. for $C_{34}H_{53}N_3O_{10}$.3HCl.2H_2O: C, 50.4; H, 7.5; N, 5.2%. Found: C, 50.6; H, 7.1; N, 5.5%. Melting Point: 174–176°C. IR: 2750 cm^{-1} (NH^+ stretch). FAB-MS (**7**).H^+ @ 664, (**7**).H_2Cl @ 703, (**7**).H_3Cl_2 @ 742.

6.3.5. N,N'-Bis[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin-16-yl)methyl]-N,N'-bis[ferroceneoxo]ethylenediamine (9)

Compound (**6**) (0.43 g, 0.69 mmol), DMAP (10 mg) and Et_3N (0.42 g, 4.14 mmol) were dissolved in CH_2Cl_2 (50 ml dry) and the solution was stirred under N_2. A solution of chlorocarbonylferrocene (**8**) (1.08 g, 4.14

mmol) in CH_2Cl_2 (50 ml) was added dropwise during 1 h. The mixture was stirred for 16 h, and then refluxed for 4 h. The solvent was then removed in vacuo and the residue redissolved in CH_2Cl_2 (100 ml). The solution was washed with water (100 ml), LiOH solution (2 M, 50 ml), HCl solution (2 M, 50 ml) and then again with water, (200 ml). The organic layer was dried over $MgSO_4$, filtered, and reduced in vacuo to yield a brown oil. The oil was eluted down a neutral alumina column with CH_2Cl_2:MeOH (99:1). The resulting red solid was eluted down a Sephadex column with methanol. The product crystallized from MeOH as a red solid, 130 mg, 18%.

^{1}H NMR ($CDCl_3$) δ: 3.48 (MeOH), 3.70 (20H, s, OCH_2CH_2O and NCH_2CH_2N), 3.87 (8H, s, Ar–OCH_2CH_2O), 4.07 (8H, s, Ar–OCH_2CH_2O), 4.14 (10H, s, cp–CH), 4.25 (4H, t, $J = 1.6$ Hz, cp–CH), 4.52 (4H, t, $J = 1.6$ Hz, cp–CH), 4.95 (4H, s, Ar–H_2–N), 6.78 (6H, m, Ar–H).

^{13}C NMR ($CDCl_3$) δ: 43.23 (NCH_2CH_2N), 60.17 (Ar–H_2N), 69.17, 69.22, 69.59 (OCH_2), 69.78 ppm (unsubstituted cp ring), 70.56, 71.11 (substituted cp ring), 77.54 (*ipso* C on cp ring), 112.56, 114.46, 119.19, 130.73, 148.54, 149.62 (Ar–C), 171.47 (C=O). Melting point: 132–133°C. IR: 1618 cm^{-1}, carbonyl stretch. FAB-MS: (**9**). H^+ @ 1045. Anal. Calc. for $C_{54}H_{64}N_2O_{12}Fe_2$ + MeOH: C, 61.38; H, 6.32; N, 2.60%. Found: C, 60.27; H, 6.05; N, 2.83%.

6.3.6. N,N'-Bis[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin-16-yl)methyl]-N,N',N''-tris[ferroceneoxo]diethylenetriamine (10)

Compound (**10**) was synthesised the way described for compound (**9**) but starting from (**7**) (0.18 g, 0.27 mmol), chlorocarbonylferrocene (1.06 g, 4.08 mmol), Et_3N (0.41 g, 4.1 mmol), CH_2Cl_2 (50 ml) and DMAP (10 mg). The product was purified by chromatography on an alumina column with CH_2Cl_2:MeOH 99.5:0.5 (v/v) as eluent. A solution in MeOH was passed through Sephadex® to give (**10**), 0.07 g, 2% yield.

^{1}H NMR ($CDCl_3$) δ: 3.76 (8H, m, CH_2CH_2O), 3.90 (4H, br, m, $ArOCH_2CH_2O$), 4.20 (18H, br, m, $ArOCH_2$ and cp–H), 4.26 (4H, br, cpH{CHCHCCO}), 4.61 (4H, br, cp–H{CHCCO}), 4.77 (4H, br, $ArCH_2NCH_2$), 4.91 (4H, br, $ArCH_2$), 6.85 (6H, br, m, Ar–H).
IR: 1612 cm^{-1}, carbonyl stretch. FAB-MS (**10**). H^+ @ 1300, (**10**). Na^+ @ 1322.

6.3.7. N,N'-Bis[(3,4-dimethoxybenzo-1-yl)methylidene]-ethylenediamine

Veratraldehyde (8.3 g, 50 mmol) was dissolved in 200 ml of THF in a two-neck flask fitted with a Dean-Stark apparatus and a dropping funnel. The solution was stirred, and a solution of ethylene diamine (1.50 g, 25 mmol) in 75 ml of THF was added dropwise. The mixture was then refluxed for 8 h as solvent was taken off from the Dean-Stark apparatus. Dry THF was occasionally added to the flask. The flask was allowed to cool, and the product crystallised as white needle-like crystals in 81% yield (7.25 g).

^{1}H NMR ($CDCl_3$) δ: 3.95 (16H, m, NCH_2CH_2N and OCH_3), 6.88 (2H, d, $^3H = 9.1$ Hz, Ar–H), 7.10 (2H, dd, $^3J = 9.1$ Hz, $^4J = 1.9$ Hz, Ar–H), 7.42 (2H, d, $^4J = 1.9$ Hz, Ar–H), 8.21 (2H, s, N=CH–). Anal. Calc. for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86%. Found: C, 67.45; H, 7.00; N, 7.77%.

6.3.8. N,N''-Bis[(3,4-dimethoxybenzo-1-yl)methylidene]-diethylenetriamine.

This compound was prepared in the way described for N,N'-bis[(3,4-dimethoxybenzo-1-yl)methylidene]ethylenediamine starting from veratraldehyde (4.15 g, 25 mmol) and diethylene triamine (1.29 g, 12.5 mmol). The product did not crystallise and so the solvent was removed in vacuo to leave a yellow oil, which was triturated with diethyl ether to give a yellow solid, 3.21 g, 64% yield.

^{1}H NMR ($CDCl_3$) δ: 1.88 (1H, br.s, NH), 2.75 (4H, s, $HNCH_2$), 3.92 (16H, m, OCH_3 and C=NCH_2), 6.82 (2H, d, $^3J = 9.1$ Hz, Ar–H), 7.10 (2H, d, $^3J = 9.1$ Hz, Ar–H), 7.35 (2H, s, Ar–H), 8.22 (2H, s, N=CH–).

6.3.9. N,N'-Bis[(3,4-dimethoxybenzo-1-yl)methyl]ethylenediamine

This compound was prepared in the way described for (**6**) but from N,N'-bis[(3,4-dimethoxybenzo-1-yl)methylidene]ethylenediamine (0.5 g, 14 mmol), $NaBH_4$ (1.07 g) and CH_3CN (60 ml). It was isolated as a yellow oil, 0.34 g, 67% yield.

^{1}H NMR ($CDCl_3$) δ:1.91 (2H, s, NH), 2.75 (4H, s, NCH_2CH_2N), 3.71 (4H, s, Ar–CH_2–N), 3.85 (12H, s, OCH_3), 6.80 (4H, br.m, Ar–H), 6.86 (2H, s, Ar–H).

6.3.10. N,N''-Bis[(3,4-dimethoxybenzo-1-yl)methyl]diethylenetriamine

The diethylene triamine analogue was prepared by reduction of the appropriate Schiff base (2 g, 5 mmol) using $NaBH_4$ (3.78 g, 0.10 mol), MeOH (35 ml) and one drop of conc HCl. The mixture was stirred for 72 h and worked up in the usual manner to give the product; 1.3 g, 65% yield.

^{1}H NMR ($CDCl_3$) δ: 2.11 (3H, br s, NH), 2.74 (8H, s, NCH_2CH_2N), 3.73 (4H, s, Ar–CH_2N), 3.64 (6H, s, OMe), 3.65 (6H, s, OMe), 6.64 (6H, br m, Ar–H).

6.3.11. N,N'-Bis[(3,4-dimethoxybenzo-1-yl)methyl]-N,N'-[ferroceneoxo]ethylenediamine (11)

To a stirred solution of N,N'-Bis[(3,4-dimethoxybenzo-1-yl)methyl]ethylenediamine (0.2 g, 0.55 mmol), DMAP (10 mg) and Et_3N (0.33 g, 3.3 mmol) in CH_2Cl_2 (30 ml) under N_2 was added dropwise a solution of chlorocarbonylferrocene (**8**) (0.85 g, 3.3 mmol) in

CH_2Cl_2 (20 ml). Compound (**11**) was then obtained in the way described for (**9**) except that NaOH solution was used in the work-up instead of LiOH. Compound (**11**) was isolated in 24% yield (0.103 g).

^{1}H NMR ($CDCl_3$) δ: 3.90 (12H, s, O*Me*), 4.20 (10H, s, C*H* ferrocene), 4.28 (4H, s, Cp–H {C*H*CHCCO}), 4.60 (4H, br.t, Cp–H {C*H*CCO}), 4.68 (4H, br.t, NCH_2), 5.05 (4H, s, NCH_2), 6.82 (6H, br m, Ar–*H*). IR: 1616 cm^{-1} carbonyl stretch. Anal. Calc. for (**11**).2MeOH: C, 64.30; H, 5.65; N, 3.57%. Found: C, 62.28; H, 6.36; N, 3.3%. FAB-MS: M^+ @ 784.

6.3.12. N,N″-Bis[(3,4-dimethoxybenzo-1-yl)methyl]-N,N′,N″-tris[ferroceneoxo]diethylenetriamine (12)

Compound (**12**) was synthesised in the way described for (**11**) but starting from the appropriate amine (0.20 g, 0.50 mmol), chlorocarbonylferrocene (1.95 g, 7.5 mmol), Et_3N (0.75 g, 7.5 mmol), CH_2Cl_2(50 ml), and DMAP (10 mg).

^{1}H NMR ($CDCl_3$) δ: 3.88 (br, O*Me*), 4.22 (Cp–*H*), 4.29 (Cp–H{C*H*CHCCO}), 4.59 (Cp–*H* {C*H*CCO}) 4.74 (NCH_2CH_2), 4.95 (br, $ArCH_2$), 6.68, 6.64, 6.75 (br m, Ar–*H*).

6.3.13. Preparation of the (9).KPF_6 Complex

A solution of compound (**9**) (0.04 g, 0.038 mmol) and KPF_6 (7 mg, 0.038 mmol) in acetonitrile (50 ml) was refluxed for 1 h. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 (10 ml). The solution was cooled to −20°C, which precipitated the complex in quantitative yield. Anal. Calc. for $C_{54}H_{64}O_{12}Fe_2N_2KPF_6$: C, 52.78; H, 5.25; N, 2.28%. Found: C, 52.26; H, 5.28; N, 2.33%.

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