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Chloride- and dihydrogenphosphate-selective anion recognition by new acyclic mono-, bis- and tris-cobaltocenium receptors

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New acyclic mono-, bis- and tris-cobaltocenium receptors containing aryl, biaryl and pyridine amide moieties have been synthesized and shown from ^{1}H NMR anion-binding studies to exhibit chloride and dihydrogenphosphate anion-selectivity preferences dependent upon the nature of the amide substituent. The single-crystal structure of a chloride complex of one of the receptors has been determined and electrochemical investigations showed that the chloride-selective cobaltocenium derivatives electrochemically sense the halide anion in acetonitrile solution.

As a consequence of the ubiquitous roles negatively charged species are known to play in numerous biological and chemical processes there is a great deal of current interest in the design and syntheses of anion receptors.[1] Of the various abiotic positively charged and neutral classes of anion receptor reported to date however, very few have the capability to *sense* anions *via* physical signalling methodologies.[2] As part of a research programme aimed at developing anion sensor technology we have recently shown that the positively charged, redox-active organometallic cobaltocenium moiety, in combination with an amide (CONH) hydrogen-bonding donor group, can complex and electrochemically recognise a variety of anions in polar organic solvent media.[3] Through variation of the number of positively charged cobaltocenium moieties and/or the nature of hydrogen-bond donor/acceptor cyclopentadienyl-appended substituents we report here the syntheses of new chloride- and dihydrogenphosphate-selective acyclic mono-, bis- and tris-cobaltocenium receptors including a single-crystal structure determination of a chloride complex of one of them.

Experimental

Instrumentation

Nuclear magnetic resonance spectra were obtained on a Bruker AM300 instrument using the solvent deuterium signal as internal reference, fast atom bombardment (FAB) mass spectra at the EPSRC mass spectrometry service, University College, Swansea. Electrochemical measurements were carried out using an E. G. and G. Princeton Applied Research 362 scanning potentiostat. Elemental analyses were performed at the Inorganic Chemistry Laboratory, University of Oxford.

Solvent and reagent pretreatment

Where necessary, solvents were purified prior to use and stored under nitrogen. Acetonitrile was predried over class 4A molecular sieves (4–8 mesh) and then distilled from calcium hydride. Unless stated to the contrary, commercial grade chemicals were used without further purification. Carboxycobaltocenium hexafluorophosphate **1**,[4] (chlorocarbonyl)-cobaltocenium chloride **4**,[4] 1,1′-bis(chlorocarbonyl)cobaltocenium chloride **6**[4] and [*N*-(*p*-aminophenyl)carbamoyl]cobaltocenium hexafluorophosphate **8**[3] were prepared according to literature procedures.

Syntheses

{*N*-[(4-*p*-Aminophenylmethyl)phenyl]carbamoyl}cobaltocenium hexafluorophosphate 2. Carboxycobaltocenium hexafluorophosphate **1** (0.3 g, 0.78 mmol) and 4,4′-methylenedianiline (0.057 g, 0.29 mmol) were dissolved in acetonitrile (20 cm^3) and the solution stirred under nitrogen. Dicyclohexylcarbodiimide (0.064 g, 0.31 mmol) was added and a white precipitate was seen to form. The mixture was stirred for 18 h after which time it was filtered and the solvent removed. The residue was washed with a small quantity of dichloromethane and purified by column chromatography [Sephadex, eluent MeCN–MeOH (3:2)]. The product was dissolved in the minimum volume of acetonitrile and then precipitated as an orange powder (yield: 220 mg, 50%) by dropwise addition of water (Found: C, 51.6; H, 4.00; N, 5.00. $C_{24}H_{22}CoF_6N_2OP$ requires C, 51.6; H, 3.95; N, 5.00%). NMR (CD_3CN): ^{1}H, δ 8.75 [1 H, s (br), CONH], 7.60 (2 H, d, J = 8.5, aryl H), 7.22 (2 H, d, J = 8.6, aryl H), 6.94 (2 H, d, J = 8.2, aryl H), 6.57 (2 H, d, J = 8.5 Hz, aryl H), 6.19 (2 H, m), 5.78 (2 H, m), 5.73 (5 H, s, all cyclopentadienyl H), 4.01 [2 H, s (br), NH_2] and 3.62 (2 H, s, CH_2); ^{13}C, δ 160.5 (C=O), 147.9 (CNH_2), 140.6 (CONH*C*), 136.5 (CH_2*C*), 130.9 (CH_2*C*), 130.5 ($C_6H_4NH_2$), 129.9 ($C_6H_4NH_2$), 121.7 (CONHC_6H_4), 116.3 (CONHC_6H_4), 96.2, 87.1, 86.1, 85.0 (all cyclopentadienyl) and 40.9 ($C_6H_4CH_2C_6H_4$). IR: $\tilde{\nu}_{max}$/cm^{-1} 3414m [N–H str (i)], 3351m [N–H str (ii)], 3121m (C–H str), 1677s [C=O str (amide I)], 1515s [C=O str (amide II)], 1414m (C–C str) and 839 (s, PF_6^-). FAB mass spectrum: m/z 413 [$M - PF_6$]$^+$.

[*N*-(6-Amino-2-pyridyl)carbamoyl]cobaltocenium hexafluorophosphate 3. Carboxycobaltocenium hexafluorophosphate **1** (0.50 g, 1.30 mmol) was dissolved in acetonitrile (40 cm^3). The mixture was stirred under nitrogen and dicyclohexylcarbodiimide (0.14 g, 0.65 mmol) was added and the mixture stirred for 30 min. A heavy white precipitate was seen to form (*N*,*N*′-dicyclohexylurea) and was filtered off. The filtrate was then added dropwise under nitrogen to a stirred solution of 2,6-diaminopyridine (0.22 g, 2.0 mmol) in acetonitrile. The mixture was stirred for 4 h during which time it became orange. The solvent was then removed by rotary evaporation and the residue washed first with water and then a small quantity of dichloromethane. The residue was then purified by column chromatography [Sephadex, eluent MeCN–MeOH (3:2)] to give the product as a green-yellow powder (yield: 100 mg, 33%) (Found: C, 41.5; H, 8.90; N, 3.30. $C_{16}H_{15}CoF_6N_3OP$ requires C, 41.0; H, 8.95; N, 3.20%). NMR (CD_3CN): ^{1}H, δ 8.76 [1 H, s (br), CONH], 7.51 (2 H, m, aryl H), 6.43 (1 H, m, aryl H), 6.22

(2 H, m), 5.78 (2 H, m), 5.74 (5 H, s, all cyclopentadienyl H) and 4.90 [2 H, s (br), NH_2]; ^{13}C, δ 165.3 (C=O), 163.7 (CONHCN), 155.0 ($NCNH_2$), 110.2, 107.9 (NCCH), 100.1 (CC=O), 92.2 and 89.7 (cyclopentadienyl). IR: $\tilde{\nu}_{max}/cm^{-1}$ 3437m [N–H str (i)], 3355m [N–H str (ii)], 3117m (C–H str), 1680s [C=O str (amide I)], 1540m [C=O str (amide II)] and 834s (PF_6^-). FAB mass spectrum: m/z 324 $[M - PF_6]^+$.

1,1′-Pyridine-2,6-diyldiiminodicarbonylbis(cobaltocenium hexafluorophosphate) 5. 2,6-Diaminopyridine (0.055 g, 0.5 mmol) and triethylamine (0.1 g, 1.0 mmol) were dissolved in dry acetonitrile (30 cm^3) and added dropwise under nitrogen to a solution of (chlorocarbonyl)cobaltocenium chloride **4** (1.06 mmol) in acetonitrile with stirring. The mixture was stirred at room temperature for 18 h during which time a green precipitate appeared over a dirty yellow solution. The precipitate was filtered off and washed with acetonitrile. It was then dissolved in a small quantity of water and aqueous ammonium hexafluorophosphate added dropwise producing an olive-green precipitate which was washed with water to give the product (yield: 0.27 g, 31%) (Found: C, 39.0; H, 3.15; N, 4.55. $C_{27}H_{23}Co_2F_{12}N_3O_2P_2$ requires C, 39.1; H, 2.80; N, 5.0%). NMR (CD_3CN): ^1H, δ 9.12 [2 H, s (br), NHCO], 8.05–7.95 (3 H, m, aryl H), 6.24 (4 H, m), 5.62 (4 H, m) and 5.77 (10 H, s, all cyclopentadienyl H); ^{13}C, δ 161.0 (C=O), 150.1 (CONHCN), 142.0 (NCCHCH), 112.2 (NCCH), 95.8 (CC=O), 87.1, 86.9 and 85.0 (all cyclopentadienyl). IR: $\tilde{\nu}_{max}/cm^{-1}$ 3637m [N–H str (i)], 3403m [N–H str (ii)], 3127s (C–H str), 1683s [C=O str (amide I)], 1529s [C=O str (amide II)] and 838 (PF_6^-). FAB mass spectrum: m/z 684 $[M - PF_6]^+$, 539 $[M - 2PF_6]^+$.

Receptor 7. 1,1′-Bis(chlorocarbonyl)cobaltocenium **6** (0.08 g, 0.19 mmol) was dissolved in acetonitrile (30 cm^3) and stirred under nitrogen. To this solution was added a solution of compound **2** (0.2 g, 0.36 mmol) and triethylamine (0.04 g, 0.4 mmol) in acetonitrile. The mixture was stirred for 40 h during which time a dark green precipitate appeared. This was filtered off, taken up in water and the product precipitated as a yellow powder by dropwise addition of aqueous ammonium hexafluorophosphate (yield: 80 mg, 28%) (Found: C, 47.5; H, 3.45; N, 3.45. $C_{60}H_{50}Co_3F_{18}N_4O_4P_3$ requires C, 48.0; H, 3.35; N, 3.75%). NMR (CD_3CN): ^1H, δ 9.26 [2 H, s (br), CONH], 8.88 [2 H, s (br), CONH′], 7.64 (4 H, d, J = 9.3, aryl H), 7.58 (4 H, d, J = 9.6, aryl H), 7.25 (4 H, d, J = 9.4, aryl H), 7.18 (4 H, d, J = 9.3 Hz, aryl H), 6.24 (4 H, m), 6.20 (4 H, m), 5.86 (4 H, m), 5.78 (4 H, m), 5.72 (10 H, s, all cyclopentadienyl H) and 3.94 (4 H, s, CH_2); ^{13}C, δ 160.7 (C=O), 160.1 (C=O), 139.4 (CONHC), 136.6 (CONHC), 130.1 (aryl CH) (two very close resonances), 121.7 (aryl CH) (two very close resonances), 97.1 (CC=O), 96.0 (CC=O), 87.7, 87.1, 86.8, 86.6, 85.1 (all cyclopentadienyl H) and 41.2 (CH_2). IR: $\tilde{\nu}_{max}/cm^{-1}$ 3402m (N–H str), 3120m (C–H str), 1674m [C=O str (amide I)], 1601m [C=O str (amide II)], 1413m (C–C str) and 840s (PF_6^-). FAB mass spectrum: m/z 1357 $[M - PF_6]^+$, 1212 $[M - 2PF_6]^+$, 1067 $[M - 3PF_6]^+$.

Receptor 9. Compound **8** (280 mg, 0.6 mmol) was powdered and dried *in vacuo*. It was then taken up in acetonitrile (30 cm^3) to give a deep red solution which was stirred under nitrogen. A solution of 1,1′-bis(chlorocarbonyl)cobaltocenium chloride (120 mg, 0.3 mmol) in acetonitrile (20 cm^3) was added dropwise and the mixture stirred for 18 h during which time a pale brown precipitate appeared. This was filtered off and washed with acetonitrile. It was then taken up in water and the product precipitated as an orange-brown powder (yield: 165 mg, 21%) by dropwise addition of aqueous ammonium hexafluorophosphate (Found: C, 41.4; H, 2.90; N, 4.10. $C_{46}H_{38}Co_3F_{18}N_4O_4P_3$ requires C, 41.8; H, 2.90; N, 4.10%). NMR (CD_3CN): ^1H, δ 9.16 [2 H, s (br), CONH], 8.87 [2 H, s (br), CONH′], 7.71 (8 H, s, aryl H), 6.25 (4 H, m), 6.19 (4 H, m), 5.92 (4 H, m), 5.79 (4 H, m) and 5.75 (10 H, s, all cyclopentadienyl H); ^{13}C, δ 160.7 (C=O), 160.2 (C=O), 135.6 (NC), 122.1 (NCC), 121.9 (NCC), 96.9, 95.8, 87.2, 86.9 and 86.6 (cyclopentadienyl). IR: $\tilde{\nu}_{max}/cm^{-1}$ 3404m (N–H str), 3126m (C–H str), 1666m [C=O str (amide I)], 1573m, [C=O str (amide II)] and 839s (PF_6^-). FAB mass spectrum: m/z 1177 $[M - PF_6]^+$, 1032 $[M - 2PF_6]^+$, 887 $[M - 3PF_6]^+$.

Crystallography

Crystal data for the chloride salt of compound **2** are given in Table 2, together with refinement details. Data were collected with Mo-Kα radiation using the MARresearch image plate system. The crystal was positioned 75 mm from the image plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[5] The structure was solved using direct methods with the SHELXS 86 program.[6] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and refined with thermal parameters equivalent to 1.2 times those of the atoms to which they were attached. The structure was then refined on F^2 using SHELXL 93.[7] All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/222.

^1H NMR titrations

A solution of the receptor (500 μl) was prepared at a concentration typically of the order of 0.01 mol dm^{-3} in deuteriated acetonitrile or dimethyl sulfoxide. The initial ^1H NMR spectrum was recorded and aliquots of anion were added by gas-tight syringe from a solution made such that 1 mole equivalent was added in 20 μl. After each addition and mixing, the spectrum was recorded again and changes in the chemical shift of certain protons were noted. The result of the experiment was a plot of displacement in chemical shift as a function of the amount of added anion, which was subjected to analysis by curve-fitting since the shape is indicative of the stability constant for the complex. The computer program EQNMR[8] was used which requires the concentration of each component and the observed chemical shift (or its displacement) for each data point.

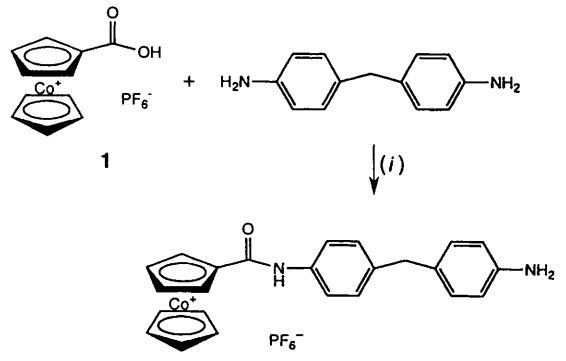
Results and Discussion

Syntheses

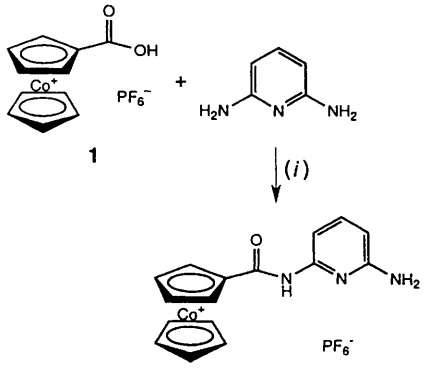
Carboxycobaltocenium hexafluorophosphate **1**[4] was treated with 4,4′-methylenedianiline in the presence of dicyclohexylcarbodiimide in acetonitrile solution to give a crude product which after purification by Sephadex LH-20-100 column chromatography using acetonitrile–40% methanol (3:2) eluent afforded compound **2** as an orange powder in 50% yield (Scheme 1). An analogous synthetic procedure with 2,6-diaminopyridine gave **3** in 33% yield (Scheme 2).

The bis(cobaltocenium) receptor **5** was prepared *via* the condensation reaction of 2 equivalents of (chlorocarbonyl)cobaltocenium chloride **4**[4] with 2,6-diaminopyridine in dry acetonitrile solution in the presence of triethylamine. The addition of an excess of ammonium hexafluorophosphate to an aqueous solution of the crude chloride salt precipitated **5** as an olive-green product in 31% yield (Scheme 3).

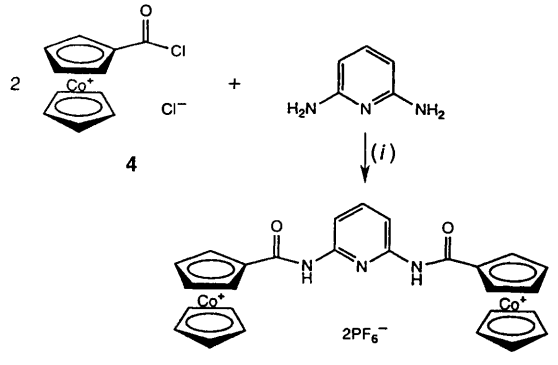
The condensation reaction of 1,1′-bis(chlorocarbonyl)cobaltocenium chloride **6**[4] with 2 equivalents of **2** in dry acetonitrile



Scheme 1 (*i*) Dicyclohexylcarbodiimide



Scheme 2 (*i*) Dicyclohexylcarbodiimide



Scheme 3 (*i*) (*a*) NEt_3, (*b*) NH_4PF_6

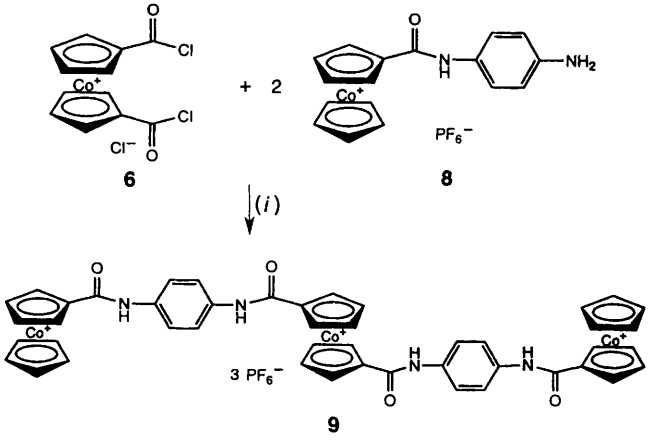
in the presence of triethylamine initially afforded a dark green product which on dissolution in water and addition of an excess of ammonium hexafluorophosphate afforded the new tris-(cobaltocenium) receptor **7** as a yellow powder in 28% yield (Scheme 4).

An analogous reaction of compound **6** with 2 equivalents of the monocobaltocenium derivative **8**[3] gave the tris(cobaltocenium) compound **9** in 21% yield (Scheme 5). All these new receptors were characterised by ^1H and ^{13}C NMR spectroscopy, elemental analyses and fast atom bombardment mass spectrometry (see Experimental section).

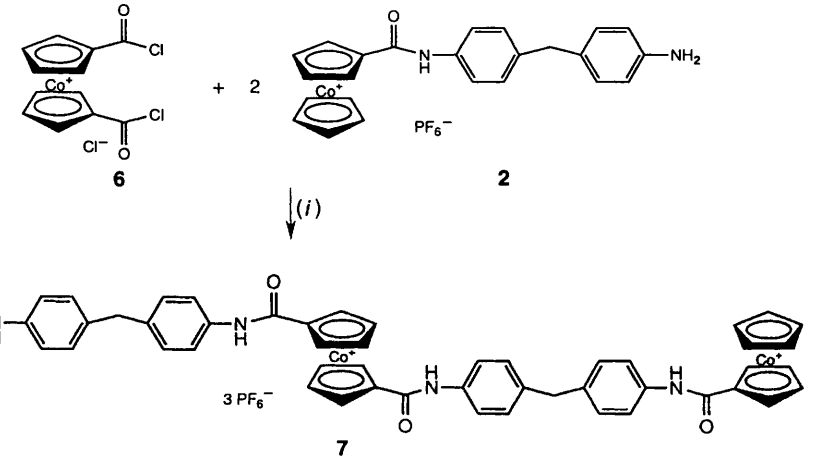
Anion co-ordination studies

Proton NMR titrations with chloride and dihydrogenphosphate anions. The addition of tetrabutylammonium chloride or dihydrogenphosphate to deuteriated acetonitrile, or because of solubility problems deuteriated Me_2SO, ^1H NMR solutions of the cobaltocenium receptors gave noteworthy and contrasting results. With the chloride anion and receptors **2**, **3** and **5** significant downfield perturbations of, in particular, the amide and cyclopentadienyl protons were observed. The resulting titration curves and Job-plot analyses (Fig. 1) suggest a cobaltocenium receptor–chloride anion stoichiometry of 1:1 in each case. Remarkably, receptor **2** on addition of dihydrogenphosphate anion exhibited virtually no shifts ($\Delta\delta \leqslant 0.05$ ppm) of any of its protons in Me_2SO solution implying that no complexation of this anion takes place. In contrast with **3** significant perturbations with $H_2PO_4^-$ were noted in the same solvent and the titration curve is shown in Fig. 2. Unfortunately in the case of **5** and $H_2PO_4^-$ immediate precipitation even in $(CD_3)_2SO$ was observed and consequently no conclusions about anion binding could be made.

Where possible the computer program EQNMR [8] was used to



Scheme 5 (*i*) (*a*) NEt_3, (*b*) NH_4PF_6



Scheme 4 (*i*) (*a*) NEt_3, (*b*) NH_4PF_6

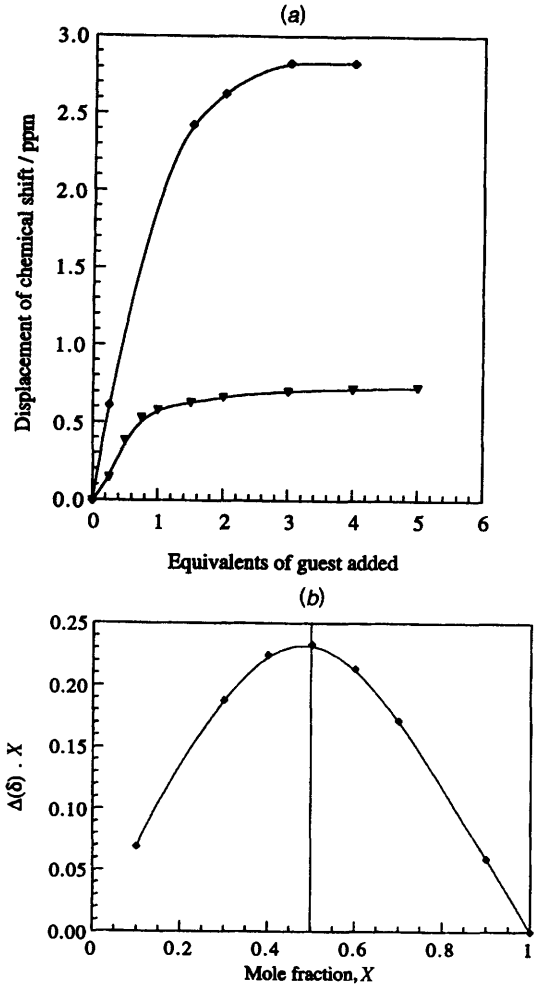


Fig. 1 (*a*) Proton NMR titration curve of receptor **2** with Cl^- in CD_3CN. ◆, Amide; ▼, cyclopentadienyl. (*b*) Job plot of chloride addition to compound **2**

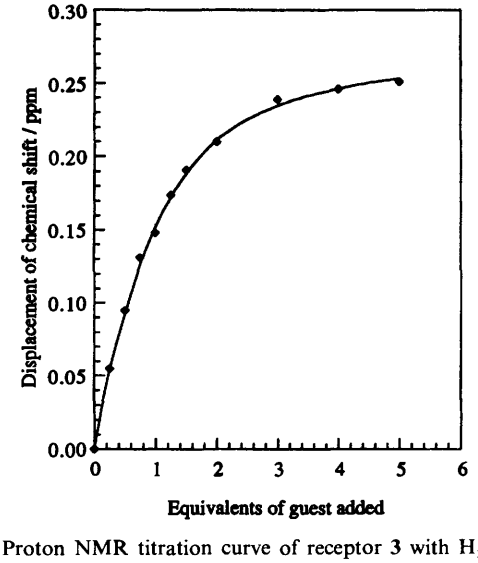


Fig. 2 Proton NMR titration curve of receptor **3** with $H_2PO_4^-$ in $(CD_3)_2SO$

estimate the stability constants from the ^1H NMR titration data and the results are summarised in Table 1. It is noteworthy that receptor **2** exhibits a pronounced selectivity preference for Cl^- over $H_2PO_4^-$ whereas the reverse selectivity trend is displayed by **3**. This latter receptor possesses a nitrogen atom in the proximity of the anion binding site which by virtue of its lone pair may furnish a repulsive interaction to the approaching chloride anion but in contrast can form an attractive hydrogen

Table 1 Anion stability constant data for compounds **2**, **3** and **5**

Receptor	Anion	Solvent	K^*/dm^3 mol^{-1}
2	Cl^-	CD_3CN	750
	$H_2PO_4^-$	$(CD_3)_2SO$	No binding
3	Cl^-	CD_3CN	60
	$H_2PO_4^-$	$(CD_3)_2SO$	250
5	Cl^-	$(CD_3)_2SO$	30
	$H_2PO_4^-$	$(CD_3)_2SO$	Precipitation

* Errors estimated to be $\leqslant 10\%$.

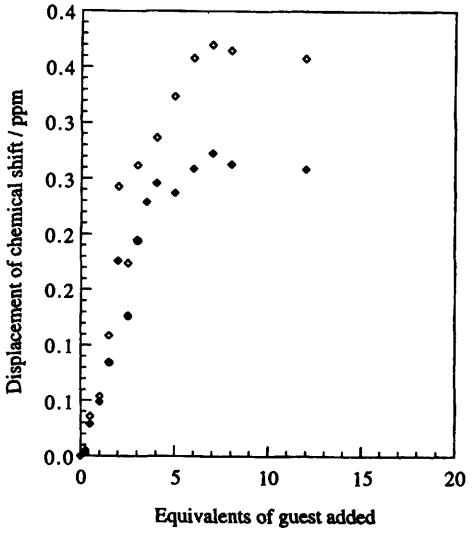
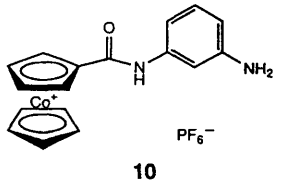


Fig. 3 Amide proton NMR titration curves of receptor **7** with Cl^- in $(CD_3)_2SO$



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bond with the $H_2PO_4^-$ anion. This selectivity trend explanation for **3** is further borne out by the related cobaltocenium derivative **10** in which the pyridine moiety has been replaced by phenyl displaying a marked chloride-anion selectivity preference over $H_2PO_4^-$, with a stability constant value for Cl^- of 770 dm^3 mol^{-1} in CD_3CN.[3]

Analogous ^1H NMR anion-titration experiments with the tris(cobaltocenium) receptors were always disappointingly thwarted with precipitation problems in CD_3CN solutions. The titration profiles with compound **7** and chloride in $(CD_3)_2SO$ solution are shown in Fig. 3. This receptor has two amide resonances in its ^1H NMR spectrum and both are significantly perturbed on addition of the halide anion. Significant downfield shifts of the cyclopentadienyl protons of up to $\Delta\delta = 0.2$ ppm were also observed. As can be seen from Fig. 3 the overall anion complexation process is complicated and unfortunately it proved impossible to establish either the stoichiometry or the stability constants from the titration data. The titration data for **9** and chloride are displayed in Fig. 4. Although it was not possible to determine stability constants from these data, quantitatively the curves suggest the stoichiometry of halide anion binding is clearly not 1:1. Interestingly ^1H NMR titrations of **7** and **9** with $H_2PO_4^-$ in $(CD_3)_2SO$ revealed no perturbations of either receptors' protons which agrees with the $H_2PO_4^-$ binding studies described earlier which noted the weak interaction between this particular anion and receptors **2** and **10**.

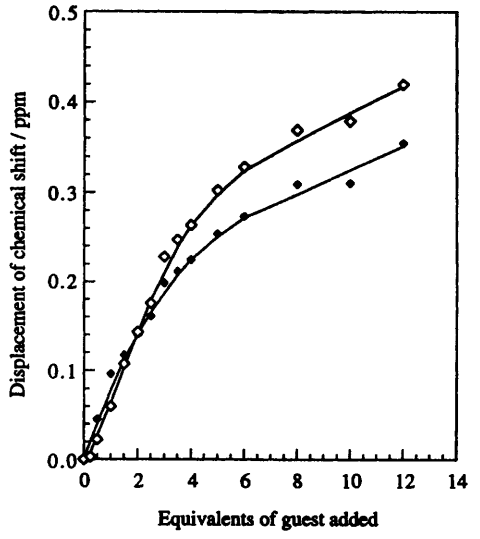

Fig. 4 Amide proton NMR titration curves of receptor **9** with Cl^- in $(CD_3)_2SO$

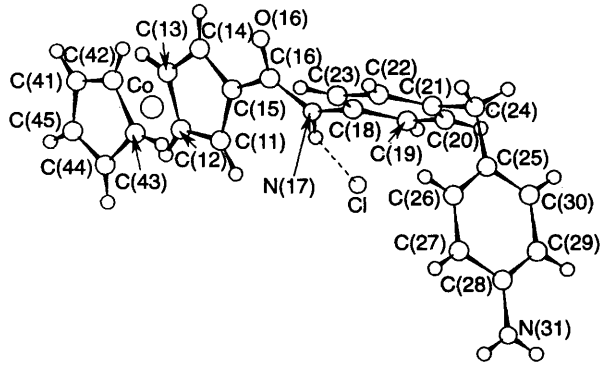

Fig. 5 Structure of the chloride complex of compound **2**

Table 2 Crystal data and structure refinement for the chloride complex of compound **2**

Empirical formula	$C_{24}H_{22}ClCoN_2O$
M	446.82
T/K	293(2)
λ/Å	0.710 70
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	9.446(7)
b/Å	11.859(7)
c/Å	18.232(9)
U/Å^3	2042(2)
Z	4
D_c/Mg m^{-3}	1.453
μ/mm^{-1}	0.987
F(000)	924
Crystal size/mm	0.25 × 0.20 × 0.30
θ range for data collection/°	2.05–25.17
hkl Ranges	0–10, −14 to 14, −21 to 21
Reflections collected	6250
Independent reflections (R_{int})	3419 (0.0588)
Weighting scheme parameters a,b*	0.50, 60.45
Data, restraints, parameters	3419, 0, 264
Goodness of fit on F^2	0.422
Final $R1$, $wR2$ for 2764 reflections	
$[I > 2\sigma(I)]$	0.0694, 0.2118
(all data)	0.0971, 0.2523
Largest difference peak and hole/e Å^{-3}	0.998, −0.704

* Weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 3 Torsion angles (°)

C(11)–C(15)–C(16)–N(17)	26.2(16)
C(15)–C(16)–N(17)–C(18)	−178.6(9)
C(16)–N(17)–C(18)–C(19)	−142.3(11)
C(20)–C(21)–C(24)–C(25)	−74.5(14)
C(21)–C(24)–C(25)–C(26)	−80.4(13)

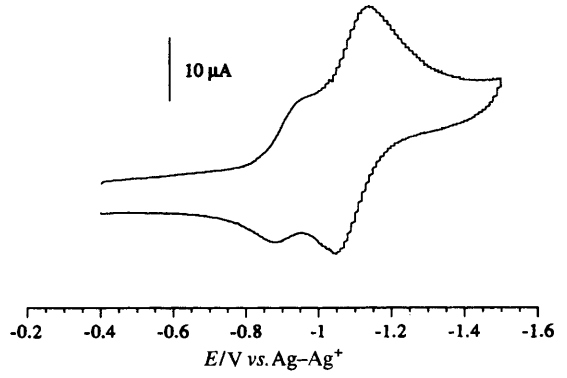

Fig. 6 Cyclic voltammogram of compound **7** in Me_2SO

X-Ray structural investigation of compound 2 with chloride as guest anion

Slow evaporation of an acetonitrile solution of compound **2** in the presence of chloride anions gave crystals suitable for an X-ray structural determination (Fig. 5).

There is an intermolecular hydrogen bond between the amide NH and the chloride anion as shown in Fig. 5 with the N(17)···Cl distance of 3.27 Å. The chloride anion also forms close contacts with C(11) at 3.54 Å and with the two amine hydrogens atoms in two different molecules [N(31) $(-x - \frac{1}{2}, 1 - y, z - \frac{1}{2})$ 3.54 and $(\frac{1}{2} + x, \frac{1}{2} - y, 2 - z)$ 3.56 Å]. Torsion angles in the molecule are shown in Table 3. They show that the constituent rings in the molecule are far from planar. Thus the C(11)–C(15)–C(16)–N(17) torsion angle of 26.2° shows that the amide group is twisted out of the plane of the cyclopentadienyl ring. The phenyl ring is not, as might be expected, coplanar with the amide group with the C(16)–N(17)–C(18)–C(19) torsion angle being −142.3°. This could well be due to presence of the chloride anion which is hydrogen bonded to N(17). As is apparent from Fig. 5, the phenylamine ring is also twisted out of the plane of this phenyl ring with C(20)–C(21)–C(24)–C(25) and C(21)–C(24)–C(25)–C(26) torsion angles of −74.5 and −80.4° respectively. The Co–C distances are in the expected range 1.97–2.03 Å.

Electrochemical anion-recognition studies

The electrochemical properties of all the new cobaltocenium derivatives were investigated in acetonitrile or Me_2SO solution using cyclic voltammetry with NBu_4BF_4 as supporting electrolyte. Each of the receptors **2**, **3** or **5** exhibited a reversible redox reduction wave in the region −0.6 to −0.95 V *vs.* Ag^+–Ag electrode (Table 4). Compounds **7** and **9** displayed two redox couples (Fig. 6) for the two different cobaltocenium moieties present in each derivative. Consideration of the respective current peak heights and the fact that 1,1′-bis-substituted cobaltocenium units are known to be easier to reduce than their monosubstituted analogues due to the presence of an additional electron-withdrawing amide unit suggests the least cathodic redox couple of the two can be assigned to the central cobaltocenium moiety (Table 4).

Cyclic voltammograms were also recorded after progressively

Table 4 Electrochemical data

Receptor	$E_{\frac{1}{2}}{}^{a}$/V	$\Delta E_{\frac{1}{2}}(Cl^-)^{b}$/mV
2	−0.91	45
3	−0.67	5
5	−0.93	5
7	−0.88,[c] −1.10[c]	5
9	−0.83,[c] −1.02[c]	5
10	−1.08	30

[a] Obtained in acetonitrile solution containing 0.2 mol dm^{-3} NBu_4BF_4 as supporting electrolyte. Solutions were *ca.* 1×10^{-3} mol dm^{-3} in receptor and potentials were obtained with reference to a $Ag–Ag^+$ electrode. [b] Cathodic shift in reduction potential produced by the presence of chloride anion (up to 10 equivalents) added as its tetrabutylammonium salt. [c] Obtained in Me_2SO.

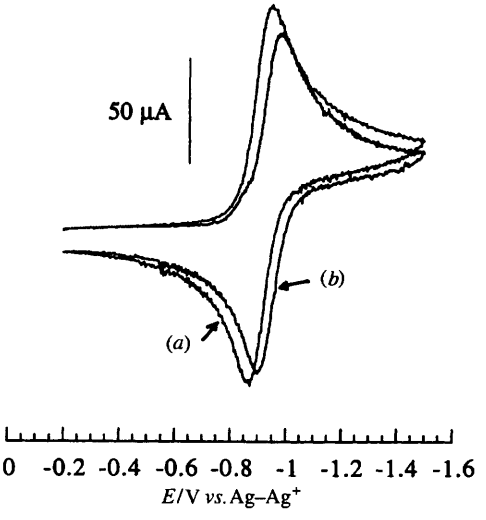

Fig. 7 Cyclic voltammograms in acetonitrile of compound **2** in the absence (*a*) and presence (*b*) of an excess of chloride anion

adding stoichiometric equivalents of chloride anion to the electrochemical solutions, and the results are also summarised in Table 4. Significant one-wave cathodic shifts of the cobaltocenium–cobaltocene redox couples of receptors **2** (Fig. 7) and **10** are observed. The binding of the halide anion increases the effective electron density on the redox centre and consequently makes reduction more difficult. In agreement with ^1H NMR titration results only small cathodic perturbations were noted with **3** and **5** even in the presence of large excess amounts of chloride anion. Only small chloride anion-induced cathodic perturbations of the redox couples of **7** and **9** were seen (Table 4) which is somewhat surprising as ^1H NMR titration studies revealed significant binding interactions with the halide anion.

Analogous electrochemical recognition experiments with $H_2PO_4^-$ all gave inconclusive results because of precipitation and electrode-adsorption problems.

Conclusion

New acyclic mono-, bis- and tris-cobaltocenium receptors containing aryl, biaryl and pyridine amide substituents have been prepared and shown to exhibit contrasting chloride and dihydrogenphosphate anion-selectivity trends.

Stability constant evaluations in acetonitrile and Me_2SO suggest receptors **2** and **10** exhibit a marked selectivity preference for Cl^- over $H_2PO_4^-$ whereas with **3** the reverse selectivity trend $H_2PO_4^- > Cl^-$ was found. The presence of the pyridine nitrogen lone pair in **3** may account for this selectivity difference. Although ^1H NMR anion-titration experiments implied the tris(cobaltocenium) receptors **7** and **9** complexed chloride anions, quantitative results could not be obtained from the titration data. It is noteworthy however that analogous ^1H NMR titrations with $H_2PO_4^-$ suggested neither receptor bound this anionic guest in Me_2SO solutions.

The single-crystal X-ray structural investigation of a chloride complex of **2** reveals the importance of hydrogen bonding in the overall anion-recognition process. Electrochemical investigations show the chloride-selective cobaltocenium receptors can sense electrochemically the halide anion in acetonitrile solution.

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