

Quantitative and Structural Investigations of Hydrogen-bonding Interactions in Anion Binding of Mono- and 1,1'-Bis-substituted Aryl Cobaltocenium Receptors†

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New acyclic monosubstituted aryl cobaltocenium derivatives, functionalised with additional hydrogen-bonding amine groups have been prepared. Quantitative investigation of the anion-binding properties by ¹H NMR spectroscopy and electrochemical methods shows enhanced binding believed to be due to amine group participation in hydrogen bonding. Similar recognition studies on 1,1'-bis-substituted aryl cobaltocenium analogues indicate an order of magnitude selectivity for the dihydrogenphosphate anion over simple halide anions. The importance of hydrogen bonding is also illustrated by the first single-crystal structure showing the anion complex of a cobaltocenium receptor.

The molecular recognition of anionic guest species² by positively charged,³ or electron-deficient neutral⁴ synthetic receptor molecules is an area of intense current research activity. Anions play essential roles in biological and chemical processes, for example, the majority of enzymes bind anions as either substrates or cofactors,⁵ and many anions act as nucleophiles, bases, redox agents and phase-transfer catalysts. We have recently reported the first redox-responsive class of anion receptor based on the pH-independent, positively charged cobaltocenium moiety and demonstrated that the simple combination of a cobaltocenium unit together with an amide N-H group are the essential components for anion recognition.¹

As an extension of this work, we report here the synthesis of new monosubstituted aryl cobaltocenium derivatives functionalised with amine groups capable of participating in hydrogen bonding. Quantitative measurement is made of the contribution of the amine group to anion complexation. Stability constant determination and electrochemical recognition studies are also performed on 1,1'-bis-substituted aryl cobaltocenium derivatives in order to investigate anion-binding selectivity. A single-crystal structure of bis-substituted derivative with bound bromide ion again highlights the importance of hydrogen bonding in recognising anions.

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 spectrometry was performed by the SERC mass spectrometry service at 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 Pre-treatment.—Where necessary, solvents were purified prior to use and stored under nitrogen.

† Anion Recognition by Acyclic Cobaltocenium Amide Receptors. Part 2. Ref. 1 is to be regarded as Part 1 of the series.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

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.

Syntheses.—[(4-Aminophenyl)aminocarbonyl]cobaltocenium hexafluorophosphate **1**. Carboxycobaltocenium hexafluorophosphate (0.40 g, 1.06 mmol) and phenylene-1,4-diamine (0.12 g, 1.11 mmol) were dissolved in acetonitrile (30 cm³) under nitrogen with stirring. 1,3-Dicyclohexylcarbodiimide (0.24 g, 1.16 mmol) was added to the stirred solution which immediately became deep red. A precipitate was also seen to form. The mixture was stirred for 24 h after which time it was filtered and the solvent removed by rotary evaporation. The residue was washed with dichloromethane (*ca.* 15 cm³) and then purified by column chromatography (Sephadex, eluent MeCN) to give the product as a brick red powder (yield 310 mg, 63%) (Found: C, 43.6; H, 4.00; N, 6.95. C₁₇H₁₆CoF₆N₂OP·0.6 dmf requires C, 44.1; H, 4.00; N, 7.10%) [ratio of product: dimethylformamide (dmf) measured from ¹H NMR integration]. ¹H NMR (CD₃CN): δ 8.60 (1 H, s br, CONH), 7.39 (2 H, d, *J* 8.7, aryl H), 6.66 (2 H, d, *J* 8.7 Hz, aryl H), 6.17 (2 H, m, cp H), 5.77 (2 H, m, cp H), 5.73 (5 H, s, cp H), 4.20 (2 H, s br, NH₂); 7.90 (s), 2.90 (s), 2.78 (s) (dmf). ¹³C NMR (CD₃CN): δ 160.0, 146.6, 128.7, 123.5, 115.2, 96.6, 87.1, 86.6, 84.6. FAB mass spectrum: *m/z* 469 (*M* + H⁺), 323 (*M* – PF₆[–]).

[(3-Aminophenyl)aminocarbonyl]cobaltocenium hexafluorophosphate **2**. Carboxycobaltocenium hexafluorophosphate (0.4 g, 1.06 mmol) and phenylene-1,3-diamine (0.12 g, 1.11 mmol) were dissolved in acetonitrile (30 cm³) to give a yellow solution. 1,3-Dicyclohexylcarbodiimide (0.24 g, 1.16 mmol) was added whereupon the solution became orange and a heavy, white precipitate formed. The mixture was stirred for 48 h and then filtered. The filtrate was evaporated to dryness under reduced pressure and the residue purified by column chromatography (Sephadex, eluent 60:40 MeCN–MeOH). Purification was carried out under nitrogen to prevent aerial decomposition of residual starting amine. The product was isolated as a yellow powder (yield 0.22 g, 45%) (Found: C, 43.4; H, 3.45; N, 5.80. C₁₇H₁₆CoF₆N₂OP requires C, 43.6; H, 3.45; N, 6.00%). ¹H NMR (CD₃CN): δ 8.57 (1 H, s br, CONH), 7.13–7.07 (2 H, m, aryl H), 6.90 (1 H, m, aryl H); 6.50 (1 H, m, aryl H), 6.19 (2 H, m,

Table 1 Crystal data and structure refinement for **3** and **5-Br⁻**

	3	5-Br⁻
Empirical formula	C ₁₇ H ₁₆ CoF ₆ N ₂ OP	C ₂₄ H ₂₂ BrCoN ₂ O ₃
<i>M</i>	468.22	525.29
<i>T</i> /K	293(2)	293(2)
λ (Mo-K α)/Å	0.710 70	0.710 70
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>P2₁/a</i>
<i>a</i> /Å	9.613(5)	10.410(6)
<i>b</i> /Å	18.700(10)	14.710(10)
<i>c</i> /Å	19.758(10)	14.494(10)
β /°		96.34(1)
<i>U</i> /Å ³	3552(5)	2206(3)
<i>Z</i>	8	4
<i>D_c</i> /Mg m ⁻³	1.751	1.726
μ /mm ⁻¹	1.128	2.635
<i>F</i> (000)	1888	1160
Crystal size/mm	0.3 × 0.15 × 0.2	0.2 × 0.2 × 0.2
θ Range/°	2.06–23.85	1.98–25.02
Index ranges	0 ≤ <i>h</i> ≤ 10, –20 ≤ <i>k</i> ≤ 21, –22 ≤ <i>l</i> ≤ 22	0 ≤ <i>h</i> ≤ 12, –16 ≤ <i>k</i> ≤ 16, –17 ≤ <i>l</i> ≤ 17
Reflections collected	8372	6041
Independent reflections	2641 [<i>R</i> (int) 0.0273]	3403 [<i>R</i> (int) 0.0189]
Refinement method	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²
Data/parameters	2638/257	3403/285
Goodness-of-fit on <i>F</i> ²	0.862	0.860
Final <i>R</i> [<i>I</i> > <i>nσ</i> (<i>I</i>)]	0.0502 (<i>n</i> = 2)	0.084 (2820 reflections) (<i>n</i> = 4)
<i>R</i> indices (all data)		
<i>R</i> 1	0.0639	0.1483
<i>wR</i> 2	0.1591	0.4296
Max., min. electron density/e Å ⁻³	0.525, –0.469	1.222, –2.818

Weighting schemes, w^{-1} : $\sigma^2(F_o)^2 + 0.003F_o^2$ for **3**; $\sigma^2(F_o)^2 + (aP)^2 + bP$ where $P = \max(F_o^2, 0) + 2F_c^2$, $a = 0.041$ and $b = 2.019$ for **5-Br⁻**.

cp H), 5.78 (2 H, m, cp H), 5.73 (5 H, s, cp H), 4.28 (2 H, s br, NH₂). FAB mass spectrum: *m/z* 323 (*M* – PF₆⁻).

[(2-Aminophenyl)aminocarbonyl]cobaltocenium hexafluorophosphate **3**. Carboxycobaltocenium hexafluorophosphate (0.4 g, 1.06 mmol) and phenylene-1,2-diamine (0.12 g, 1.11 mmol) were dissolved in dry acetonitrile (30 cm³) under nitrogen with stirring. 1,3-Dicyclohexylcarbodiimide (0.24 g, 1.16 mmol) was added to the solution which became orange. A white precipitate was also seen to form. The mixture was stirred for 18 h then filtered and the filtrate evaporated to dryness. Preliminary purification of the residue was carried out by column chromatography (Sephadex: eluent 60:40 MeOH–MeCN). The compound was then taken up in boiling methanol and ≈5% water added. On standing, the product formed as large yellow crystals, suitable for X-ray analysis (yield 0.2 g, 40%) (Found: C, 43.7; H, 3.35; N, 5.80. C₁₇H₁₆CoF₆N₂OP requires C, 43.6; H, 3.45; N, 6.00%). ¹H NMR (CD₃CN): δ 8.70 (1 H, s br, CONH), 7.22 (1 H, d, aryl H), 7.12 (1 H, t, aryl H), 6.87 (1 H, d, aryl H), 6.77 (1 H, t, aryl H), 6.22 (2 H, m, cp H), 5.81 (2 H, m, cp H), 5.77 (5 H, s, cp H), 4.30 (2 H, s br, NH₂). FAB mass spectrum: *m/z* 323 (*M* – PF₆⁻).

Crystal Structure Determination of 3 and 5-Br⁻.—Crystal data for **3** and **5-Br⁻** are given in Table 1, together with refinement details. Data for both crystals were collected with Mo-K α radiation using the MAR research image plate system. The crystals were positioned at 75 mm from the image plane. 95 Frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.⁶ Both structures were solved using direct methods with SHELX 86.⁷ In both structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on carbon and nitrogen were included in calculated positions in both structures. The hydrogen atoms of the water molecule in **5-Br⁻** could not be located and the high agreement factor observed was due to poor crystal quality. Both structures were refined using SHELXL.⁸ Calculations were carried out using a

Table 2 Atomic coordinates ($\times 10^4$) for compound **3**

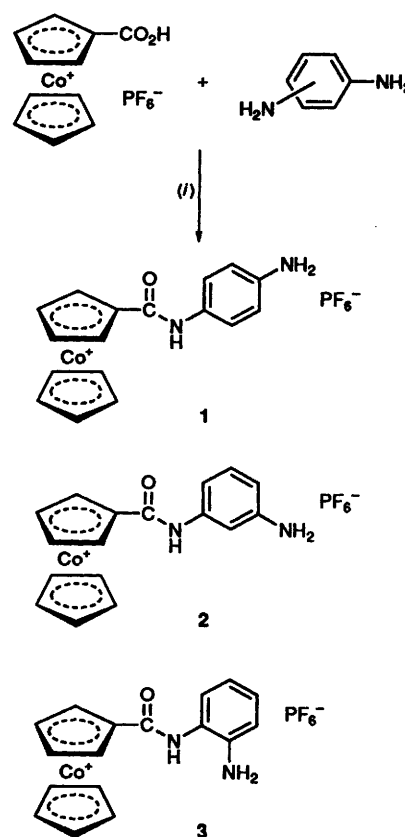
Atom	<i>x</i>	<i>y</i>	<i>z</i>
Co	434(1)	1 258(1)	8 705(1)
P(1)	969(1)	2 245(1)	11 066(1)
F(1)	2 091(4)	2 177(3)	11 628(2)
F(2)	–176(4)	2 185(3)	11 622(2)
F(3)	941(7)	3 070(2)	11 181(2)
F(4)	931(8)	1 429(3)	10 960(3)
F(5)	–167(4)	2 330(2)	10 506(2)
F(6)	2 103(5)	2 349(4)	10 527(2)
C(11)	–1 359(5)	759(2)	8 916(2)
C(12)	–608(6)	888(3)	9 506(2)
C(13)	664(6)	553(3)	9 453(2)
C(14)	738(5)	208(2)	8 824(2)
C(15)	–528(4)	331(2)	8 489(2)
C(21)	1 683(6)	2 081(3)	8 900(3)
C(22)	2 180(5)	1 688(3)	8 346(3)
C(23)	372(6)	2 322(3)	8 746(3)
C(24)	44(7)	2 099(3)	8 109(3)
C(25)	1 168(7)	1 708(3)	7 863(3)
C(16)	–980(4)	109(2)	7 805(2)
O(17)	–2 046(3)	346(2)	7 569(2)
N(18)	–190(4)	–370(2)	7 495(2)
N(31)	–2 549(4)	–1 187(2)	7 134(2)
C(31)	–430(4)	–587(2)	6 820(2)
C(32)	525(5)	–412(3)	6 337(3)
C(33)	320(6)	–615(3)	5 677(3)
C(34)	–841(6)	–975(3)	5 507(3)
C(35)	–1 781(5)	–1 157(2)	5 980(2)
C(36)	–1 586(4)	–986(2)	6 657(2)

Silicon Graphics R4000 workstation at the University of Reading. The final atomic coordinates for **3** and **5-Br⁻** are given in Tables 2 and 3 respectively.

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

Table 3 Atomic coordinates ($\times 10^4$) for structure **5-Br⁻**

Atom	x	y	z
Co(1)	3097(2)	4289(1)	3166(1)
C(11)	3325(14)	4067(11)	4542(10)
C(12)	2349(13)	4753(10)	4314(8)
C(13)	1415(12)	4347(10)	3679(12)
C(14)	1732(15)	3422(11)	3560(11)
C(15)	2901(16)	3251(9)	4058(10)
C(16)	2513(15)	5685(9)	4709(12)
O(17)	3557(9)	5933(8)	5044(7)
N(18)	1432(12)	6160(8)	4633(7)
C(19)	1263(13)	7077(10)	4987(8)
C(20)	149(16)	7474(13)	4743(13)
C(21)	-141(19)	8327(11)	5098(15)
C(22)	849(18)	8796(16)	5664(13)
C(23)	1982(24)	8344(13)	5905(13)
C(24)	2227(17)	7492(11)	5572(10)
C(31)	3227(19)	3982(11)	1801(10)
C(32)	3964(15)	5332(11)	2551(9)
C(33)	2932(18)	4959(14)	1948(10)
C(34)	4874(16)	4623(12)	2833(13)
C(35)	4422(17)	3782(15)	2365(13)
C(36)	4000(14)	6282(10)	2887(9)
O(37)	3052(10)	6759(8)	2920(10)
N(38)	5185(12)	6569(9)	3169(9)
C(39)	5494(15)	7472(10)	3530(10)
C(40)	6467(17)	7925(13)	3232(15)
C(41)	6746(26)	8831(17)	3567(19)
C(42)	6153(29)	9091(18)	4201(23)
C(43)	5177(23)	8679(14)	4553(19)
C(44)	4851(19)	7819(14)	4207(12)
Br(1)	-1744(1)	4431(1)	6682(1)
O(2)	-509(15)	3376(12)	8014(11)

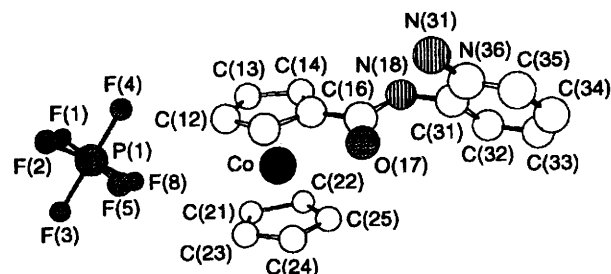
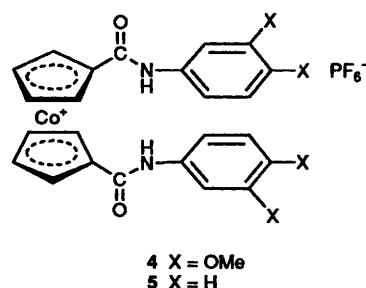
**Scheme 1** (i) 1,3-Dicyclohexylcarbodiimide, MeCN

Results and Discussion

Syntheses.—The new monosubstituted aryl cobaltocenium derivatives **1–3** were prepared *via* the condensation of carboxycobaltocenium hexafluorophosphate⁹ and one equivalent of the appropriate phenylenediamine, in the presence of the coupling agent 1,3-dicyclohexylcarbodiimide, in dry acetonitrile solution (Scheme 1).¹⁰ The crude products were purified using Sephadex column chromatography in yields ranging from 40 to 63%. The syntheses of the 1,1'-bis-substituted aryl cobaltocenium compounds 1,1'-bis[(3,4-dimethoxyphenyl)aminocarbonyl]cobaltocenium hexafluorophosphate **4*** and 1,1'-bis(phenylaminocarbonyl)cobaltocenium hexafluorophosphate **5** have recently been described.¹

X-Ray Structural Investigation of 3.—Yellow crystals of **3** suitable for X-ray structural investigation were grown from a methanol–water solution of the compound. The structure shows almost eclipsed cyclopentadienyl rings (Fig. 1) and there is a hydrogen-bonding interaction between the amine and a fluorine atom of the anion in an adjacent structural subunit. No interaction of the amide group is observed.

Anion Co-ordination Studies.—Stability constant determinations from ¹H NMR titrations. Mono-arylamide cobaltocenium receptors **1–3**. The addition of tetrabutylammonium chloride to deuterated acetonitrile ¹H NMR solutions of **1–3** resulted in significant shifts of the respective protons of all three receptors. Substantial downfield shifts of the amide (Fig. 2) and cyclopentadienyl protons are noteworthy. The resulting titration curves suggest a cobaltocenium receptor–chloride anion stoichiometry of 1:1 (Fig. 3). The computer program EQNMR¹¹ was used to estimate the stability constants from

**Fig. 1** Structure of compound **3**

the ¹H NMR titration data and the results are summarised in Table 4. The observed order of decreasing stability **2** > **3** > **1** may be explained by considering the additional favourable hydrogen-bonding interactions between the chloride ion and the primary amine group; this amine function is sterically accessible for **2** and **3** but not for **1** (Fig. 3). The *para*-substituted NH₂ group of **1** cannot participate intramolecularly in hydrogen bonding to a closely bound chloride guest anion and hence there is an order of magnitude difference in stability constant between receptor **1** and receptors **2** and **3**.

1,1'-Bis-arylamide cobaltocenium receptors **4** and **5**.

* As the BPh₄⁻ salt in ref. 1. The PF₆⁻ salt was obtained by anion exchange.

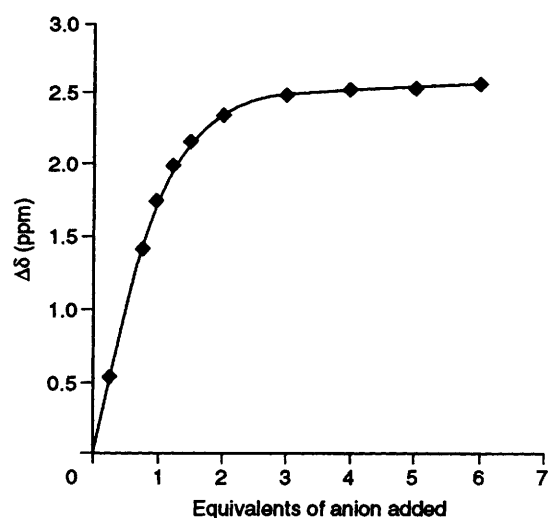


Fig. 2 Proton NMR titration curve of receptor 2 and Cl^- in CD_3CN ; $\Delta\delta$ is the shift difference of the amide proton

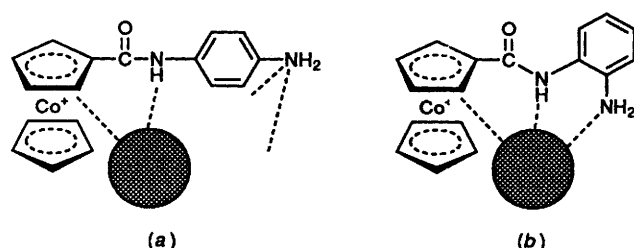


Fig. 3 Schematic representation of chloride complexes of 1 (a) and 3 (b) illustrating the possibility of additional hydrogen-bonding interactions from the amino group of 3

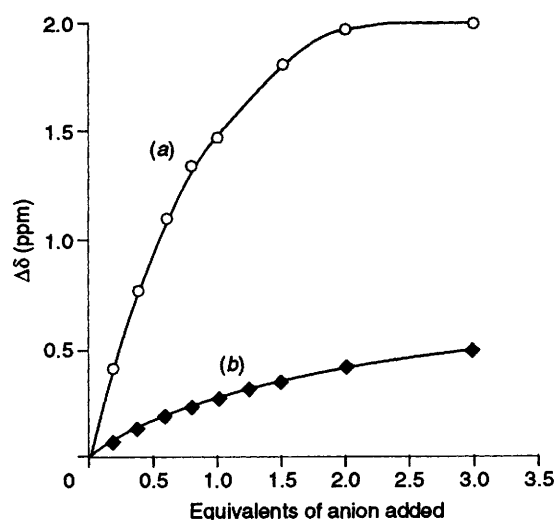


Fig. 4 Proton NMR titration curve of receptor 5 with H_2PO_4^- (a) and Cl^- (b) in $(\text{CD}_3)_2\text{SO}$; $\Delta\delta$ is the shift difference of the amide proton

Analogous ^1H NMR titration experiments were carried out with 4 and 5 with tetrabutylammonium chloride, bromide and dihydrogenphosphate salts in deuteriated dimethyl sulfoxide (Fig. 4). Solubility problems necessitated the use of $(\text{CD}_3)_2\text{SO}$ as solvent. The stability constant data for a cobaltocenium receptor–anion stoichiometry of 1:1, obtained from EQNMR titrimetric curve analysis are shown in Table 5.

Comparing Tables 4 and 5, as expected, the magnitudes of the anion stability constants obtained in the more polar $(\text{CD}_3)_2\text{SO}$

Table 4 Stability constant data for 1–3 and chloride anion in CD_3CN

Complex	$K^*/\text{dm}^3 \text{mol}^{-1}$
1	24
2	770
3	630

* Errors estimated to be $\leq 5\%$.

Table 5 Stability constant data for 4 and 5 with various anions in $(\text{CD}_3)_2\text{SO}$

Complex	Anion	$K^*/\text{dm}^3 \text{mol}^{-1}$
4	Cl^-	30
4	Br^-	25
5	Cl^-	35
5	Br^-	25
5	H_2PO_4^-	320

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

Table 6 Hydrogen-bonding parameters* for 5- Br^-

	Atoms	H–Br distance/Å	Angle/°
cp H	C(13)–H(13)–Br(1)	2.876	154
N–H	N(18)–H(18)–Br(1)	2.898	164
Aryl H	C(20)–H(20)–Br(1)	3.022	155
N–H	N(38)–H(38)–Br(1')	2.690	158
cp H	C(34)–H(34)–Br(1')	3.024	139

Br(1') is related to Br(1) by $1 + x, y, z$. Positions of hydrogen atoms are calculated. * For a discussion of C–H...X bonding see ref. 13.

solvent (relative permittivity $\epsilon = 46.7$) are generally smaller than those determined in CD_3CN ($\epsilon = 34$) solution. Within experimental error no selectivity is exhibited by 4 or 5 for either chloride or bromide guest anions. However, the K value for receptor 5 with dihydrogenphosphate is an order of magnitude greater than for the corresponding halide complexes; similar selectivity has been previously observed.¹²

X-Ray Structural Investigation of 5 with Bromide as Guest Anion, 5- Br^- .—Slow evaporation of an acetonitrile–water solution of 5 in the presence of bromide anions gave crystals suitable for an X-ray structural determination. Fig. 5 shows the structure of the complex in which the bromide anion is hydrogen bonded to the amide (N–H), cyclopentadienyl (cp H) and aryl (aryl H) protons (Table 6). The two cyclopentadienyl rings are almost eclipsed and one phenyl group is almost coplanar to the cp ring whilst the other is perpendicular. The crystal packing is such that the anion complex consists of one bromide anion per receptor molecule, with each bromide anion hydrogen bonded to two amide protons, one from each of two separate receptor molecules (Fig. 6). Water is also observed in the unit cell but the positions of its hydrogen atoms cannot be calculated. It is, however, believed to participate in hydrogen bonding with the bromide anion.

The linkage between the cp and phenyl rings varies in conformation between structures 3 and 5- Br^- . Also, between the two parts of 5- Br^- , there is a considerable difference in torsion angle. There would therefore appear to be relatively free rotation about the N–C bond in the linkage.

Electrochemical Anion–Recognition Studies.—The electrochemical properties of all the new acyclic cobaltocenium derivatives were investigated in acetonitrile using cyclic voltammetry with NBu_4BF_4 as the supporting electrolyte. Each compound exhibited a reversible redox reduction wave in the region -0.8 to -1.10 V vs. Ag^+/Ag electrode (Table 7). The bis-substituted cobaltocenium units were easier to reduce than

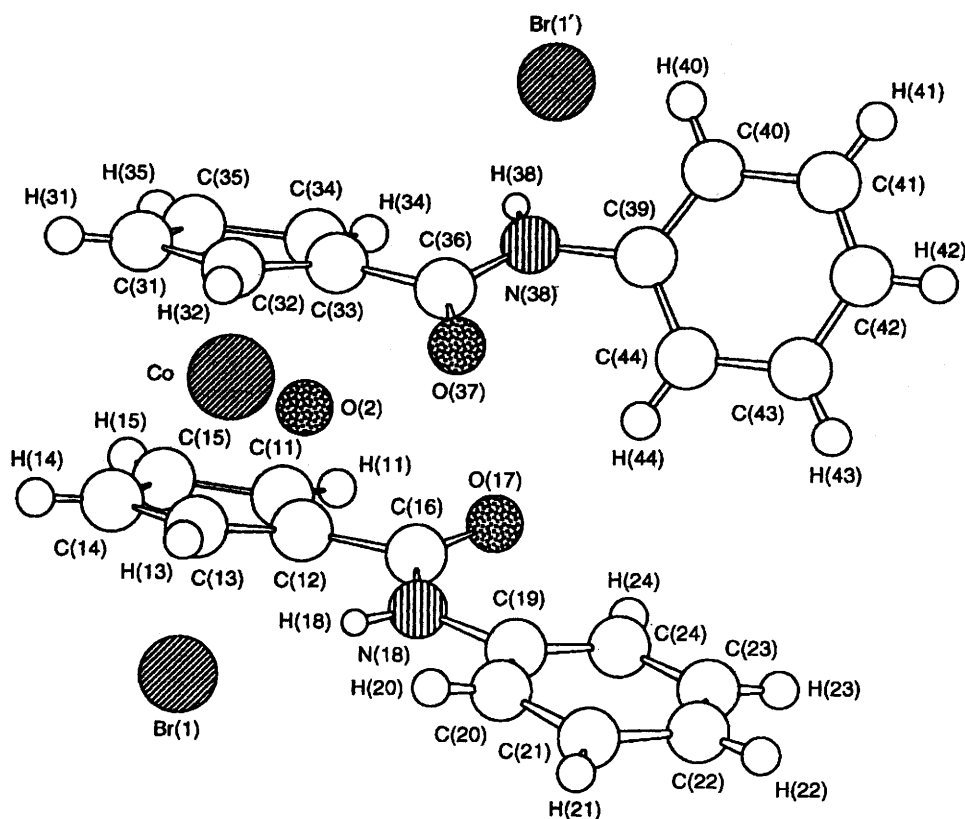
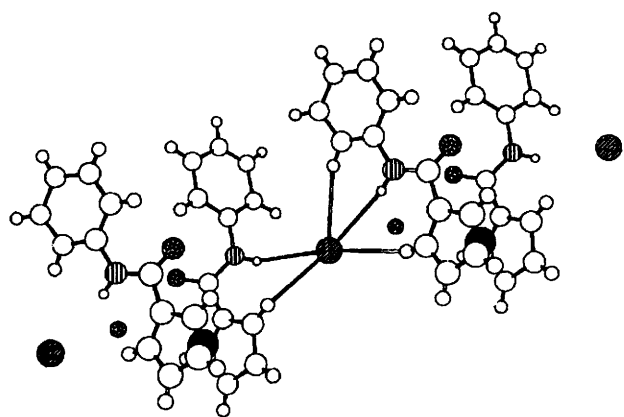
Fig. 5 Structure of 5-Br⁻ including water of crystallisationFig. 6 Structure of 5-Br⁻ illustrating the whole environment of the bromide anion

Table 7 Electrochemical data

Complex	E_1/V^a	Anion	$\Delta E_1/mV^b$
1	-1.10	Cl ⁻	35
2	-1.08	Cl ⁻	30
3	-1.03	Cl ⁻	55
4	-0.80	Cl ⁻	90
4	-0.80	Br ⁻	40
4	-0.80	H ₂ PO ₄ ⁻	240
5	-0.83	Cl ⁻	85
5	-0.83	H ₂ PO ₄ ⁻	240

^a Obtained in acetonitrile solution containing 0.2 mol dm⁻³ NBu₄BF₄ 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 presence of anions (up to 10 equivalents) added as their tetrabutylammonium salts.

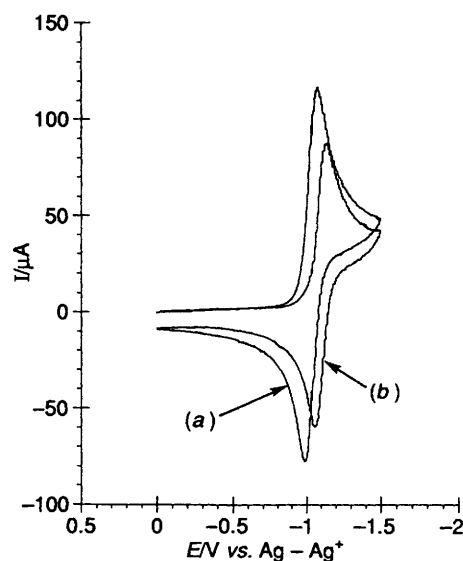


Fig. 7 Cyclic voltammograms in acetonitrile of 3 in the absence (a) and presence (b) of excess chloride ion

the monosubstituted due to the presence of an extra electron-withdrawing amide unit. Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of anion guests to the electrochemical solutions, and the results are also summarised in Table 7. Significant one-wave cathodic shifts of the cobaltocenium-cobaltocene redox couples of receptors 1-5 are observed with all anionic guest species (Fig. 7). The complexed anion effectively stabilises the positive charge of the cobaltocenium unit. It is noteworthy that the largest magnitudes of cathodic perturbation are observed with the H₂PO₄⁻ anion guest, i.e. 240 mV with 4 and 5. This result complements the stability constant data (Table 5) in which the highest *K* values are obtained with H₂PO₄⁻.

Conclusion

New acyclic monosubstituted aryl cobaltocenium derivatives containing *para*-, *meta*- and *ortho*-substituted amine groups have been prepared and shown to co-ordinate the chloride anion. Stability constant evaluations in acetonitrile suggest enhanced strength of chloride-ion binding resulting from additional favourable amine-halide hydrogen-bonding interactions which are sterically accessible for **2** and **3** but not for **1**.

1,1'-Bis-substituted aryl cobaltocenium compounds **4** and **5** form solution anion complexes with Cl^- , Br^- and H_2PO_4^- with **5** exhibiting the largest magnitude of stability constant for H_2PO_4^- [$K = 320 \text{ dm}^3 \text{ mol}^{-1}$ in $(\text{CD}_3)_2\text{SO}$]. The first single-crystal X-ray structural investigation of a cobaltocenium receptor-anion complex (**5**· Br^-) highlights the importance of hydrogen bonding in the binding of anions. Electrochemical investigations reveal that these relatively simple amide-substituted cobaltocenium systems can electrochemically recognise a variety of anions with H_2PO_4^- producing the largest magnitude of cathodic perturbation.

Acknowledgements

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References

- 1 P. D. Beer, C. Hazlewood, D. Hesek, J. Hodacova and S. E. Stokes, *J. Chem. Soc., Dalton Trans.*, 1993, 1327.
- 2 B. Dietrich, *Pure Appl. Chem.*, 1993, **65**, 1457; J.-L. Pierre and P. Baret, *Bull. Soc. Chim. Fr.*, 1983, 367; B. Dietrich, in *Inclusion Compounds*, eds J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, New York, 1984, vol. 2, p. 337; F. P. Schmidtchen, *Nachr. Chem. Tech. Lab.*, 1988, **36**, 8.
- 3 M. W. Hosseini, A. J. Blacker and J.-M. Lehn, *J. Am. Chem. Soc.*, 1990, **112**, 3896 and refs. therein; F. P. Schmidtchen, *J. Org. Chem.*, 1986, **51**, 5161; P. D. Beer, J. W. Wheeler, A. Grieve, C. Moore and T. Wear, *J. Chem. Soc., Chem. Commun.*, 1992, 1225.
- 4 H. E. Katz, *Organometallics*, 1987, **6**, 1134; J. D. Wuest and B. Zacharie, *J. Am. Chem. Soc.*, 1987, **109**, 4714; M. T. Blandon, J. N. Horner and M. Newcomb, *J. Org. Chem.*, 1989, **54**, 4626; M. T. Reetz, C. M. Niemeyer and K. Harms, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1472; D. M. Rudkevich, W. P. R. V. Staathamer, W. Verboom, J. F. J. Engbersen, S. Harkema and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1992, **114**, 9671.
- 5 L. G. Lang, J. F. Riordon and B. L. Vallee, *Biochemistry*, 1974, **13**, 4361.
- 6 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
- 7 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 8 G. M. Sheldrick, SHELXL, personal communication, 1993.
- 9 J. E. Sheats and M. D. Rausch, *J. Org. Chem.*, 1970, **35**, 3245.
- 10 J. C. Sheehen and G. P. Hess, *J. Am. Chem. Soc.*, 1955, **77**, 1067.
- 11 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311.
- 12 P. D. Beer, Z. Chen, A. J. Goulden, A. R. Graydon, S. E. Stokes and T. Wear, *J. Chem. Soc., Chem. Commun.*, 1993, 1834; D. N. Reinhoudt, S. Valiayaveetil, J. F. J. Engbersen and W. Verboom, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 900.
- 13 T. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1993, **115**, 4540.

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