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Alkali-metal binding properties of simple ferrocenyl- and ruthenocenyl-substituted aza-crown ethers

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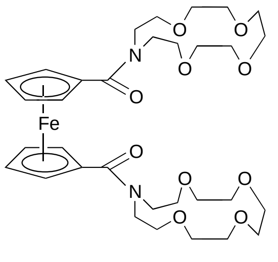
Reaction of 1-chlorocarbonyl-ferrocene or -ruthenocene with aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) afforded the respective amide-linked metallocene crowns. Nucleophilic displacement of trimethylamine from trimethylammoniomethyl-ferrocene or -ruthenocene iodides with aza-15-crown-5 yielded the corresponding methylene-linked crowns. Variable-temperature ^{13}C NMR investigation of the hindered rotation about the amide links of the amide-linked crowns in the presence of guest cations indicated that cation complexation occurs exclusively within the crown ring. Extraction experiments with a range of metal-cation dye salts revealed a favourable binding capacity for the methylene-linked crowns. Detailed ^{13}C NMR analysis of sodium and potassium ion binding by these systems suggests the presence of a stabilising interaction between the metallocene π system and the crown-bound cation. Cyclic voltammetric analysis of metal-ion binding by the amine-linked crowns revealed cation-induced shifts of the appropriate redox couple comparable with those reported for related systems.

Prompted by the undeniable attraction of developing host molecules capable of exhibiting a selective electrochemical response to the presence of a guest cation, redox-active ionophores based on covalently linked crown ether–metallocene systems have received much attention in recent years.[1–5] In spite of the rather limited structural variation offered by the attachment of simple crown ether rings to metallocene units a variety of modes of complexation of metal cations have been identified for such systems. Some of the first metallocenylcryptands, containing amide links between the ionophore and metallocene, were found to bind cations *via* their carbonyl functions rather than within the crown ring.[6] Simple metallocene–crown conjugates tended to behave more predictably with cation coordination occurring *via* the crown ring system.[7] Additionally, there is evidence that transition-metal-ion binding by certain ferrocenylcryptands involves a direct, stabilising ferrocenyl iron–cation interaction.[8] Such observations prompted the synthesis and investigation of a series of simple metallocene crowns **9**, **10**, **15** and **16**. Our aim was not to target a particular guest cation or attempt to tune any electrochemical response, rather we hoped to examine in some detail the factors involved in the binding of guest cations by an investigation of the behaviour of some constitutionally simple members of this much studied class of materials.

Results and Discussion

Syntheses

Following well established methods[7] reaction of 1-(chlorocarbonyl)-ferrocene **7** or -ruthenocene **8** with aza-15-crown-5 in the presence of NEt_3 gave the respective amido-linked metallocene crowns **9** and **10** after chromatographic purification. The methylene-linked analogues **15** and **16** were prepared from the quaternary ammonium metallocene salts **13** and **14** by nucleophilic displacement using aza-15-crown-5 in the presence of K_2CO_3 (the ammonium salts having been obtained by quaternisation of dimethylaminomethylmetallocenes **11** and **12** with MeI). Whilst the dimethylamine derivative **11** is commercially available, its ruthenocene analogue **12** must be prepared by the Mannich reaction of ruthenocene with $Me_2NCH_2NMe_2$ using a procedure analogous to that described for **11**. The conversion into **14** proved rather less efficient (38%) than that for its ferrocene analogue, a reflection of the generally lower aromatic reactivity of ruthenocene towards electrophilic species.[9] Scheme 1 summarises the synthetic routes.



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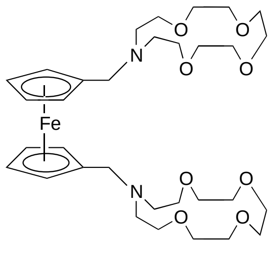

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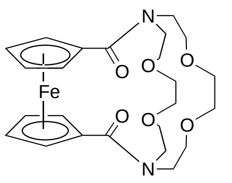

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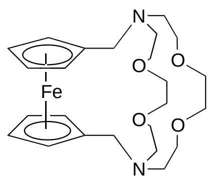

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All new compounds were fully characterised by ^{1}H and ^{13}C NMR spectroscopy and either high-resolution FAB mass spectrometry or elemental analysis (see Experimental section).

Variable-temperature (VT) ^{13}C NMR spectroscopy

The temperature dependence of NMR spectra can be used to obtain information about internal energy barriers to rotation within a molecule. The restricted rotation about the C−N bond of an amide linkage is the classical example of a dynamic process that can be studied using this technique.[10] Resonance theory predicts a certain degree of double-bond character for the C−N link, with an associated increase in the barrier to rotation over that observed for strict single C−N bonds such as those found, for example, in amines. On the chemical shift timescale it is possible to freeze this rotation and observe coalescence phenomena as the temperature is increased. Readily measured parameters allow calculation of the energy barrier to rotation (see Experimental section).

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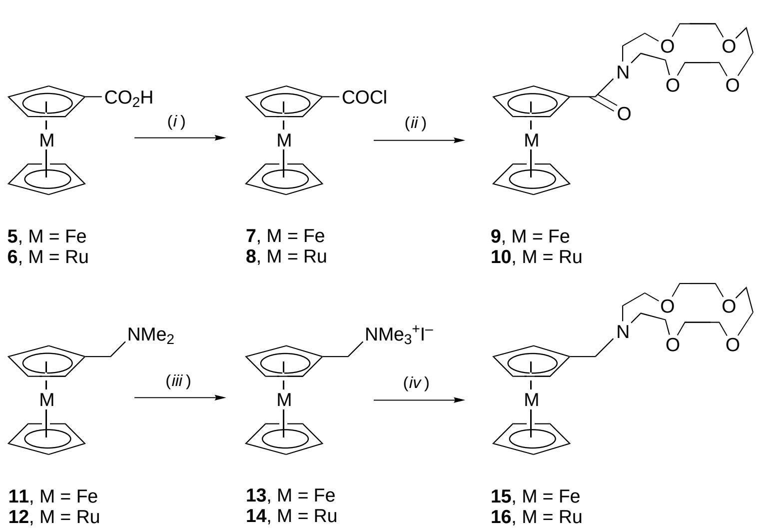

Scheme 1 (*i*) $(COCl)_2$, CH_2Cl_2, dimethylformamide (dmf) (catalyst); (*ii*) aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane), NEt_3, benzene; (*iii*) MeI, MeOH; (*iv*) aza-15-crown-5, K_2CO_3, MeCN

The activation barrier for amide rotation in the ferrocene bis(crown) **1** has been reported elsewhere ($\Delta G^{\ddagger} = 65.0$ kJ mol^{-1}, no error quoted),[7] a value typical of a ferrocene-linked amide bond.[11] Additional experiments performed in the presence of stoichiometric amounts of metal salts revealed that the presence of sodium ions lowered this barrier by around 5 kJ mol^{-1} whereas in the case of lithium ions it was increased by 2.5 kJ mol^{-1}. These observations were presented as supporting evidence for different modes of complexation of the bis(crown) with various metal cations. From solid-state complexation studies, sodium ions are known to reside within the crown ether rings of **1** where they will attract electron density from the amide nitrogen thus weakening the bond and lowering the rotation energy barrier. In contrast, lithium ions are known to co-ordinate externally to the two amide carbonyl groups in such structures, further polarising the C–O bond, thereby increasing the double-bond character of the C–N bond and raising the activation energy to rotation.

The VT NMR technique has now been applied to metallocene amido-crowns **9** and **10** in order to determine whether a single binding mode was operating. Variable-temperature ^{13}C NMR spectra were recorded using CD_3CN solutions of the crowns at 91 MHz. The coalescence temperatures (T_c), frozen-condition frequency separations ($\Delta\nu$) and activation energy barriers ($\Delta G^{\ddagger}$) obtained from the variable-temperature experiments are summarised in Table 1. These results show reasonable agreement with the barriers to rotation observed for ferrocene bis(crown) **1** (65.0 kJ mol^{-1}) and its ruthenocene analogue (64.1 kJ mol^{-1}). They support previously reported observations[11] that an amido substituent on one metallocene ring has negligible effect on a substituent on the other, and that the nature of the metallocene has little effect on the value of the rotation barrier (values for ferrocene derivatives are consistently *slightly* higher than those obtained for the equivalent ruthenocene compounds, again perhaps reflecting the more electron-rich nature of the ferrocene unit).

Further ^{13}C VT NMR experiments were conducted with ferrocene crown **9** in the presence of lithium and sodium ions (added as their perchlorate salts). The results are summarised in Table 2. The addition of both metals is seen to reduce the activation energy barrier to rotation by around 3 kJ mol^{-1}. Following the argument discussed previously, this behaviour is consistent with the binding of each of the metal cations within the crown cavity where the electrostatic attraction between the amide nitrogen and the metal cation lowers the electron density associated with the C–N bond, thus lowering the rotational energy barrier. The observation that the rotation barrier is *lowered* in the presence of lithium ions is in direct contrast with the situation found in metallocene *bis*(crowns) such as **1**. This result suggests that a necessary prerequisite for metal-ion binding *outside* the crown cavity is the presence of two carbonyl groups and that for the simple *mono*crowns described here only the crown cavity itself provides a suitable metal-ion binding site.‡

Table 1 Summary of ^{13}C VT NMR experimental data

Crown	T_c[a]/K	$\Delta\nu$/Hz	$\Delta G^{\ddagger}$[b]/kJ mol^{-1}
9	310 ± 5	65	63.2 ± 1.0
10	314 ± 5	123	62.4 ± 1.0

[a] Error involved in determining T_c from spectral inspection. [b] Error associated with coalescence temperature accuracy of ±5 K.

Table 2 Results of ^{13}C VT NMR experiments in the presence of metal ions

Experiment	$\Delta G^{\ddagger}$[a]/kJ mol^{-1}
9	63.4 ± 1.0
9 + $LiClO_4$[b]	60.0 ± 1.0
9 + $NaClO_4$[b]	59.9 ± 1.0

[a] Error involved in determining T_c from spectral inspection, ±5 K. [b] Addition of 1 molar equivalent of metal salt.

Assessment of metal-ion extraction ability using oxonol dyes

The picrate-salt extraction technique devised by Cram has become a widely employed method for the screening of ligands for their ability to bind metal ions.[12–15] The method is based on monitoring the transfer of picrate anion from an aqueous to an organic phase. This transfer accompanies the extraction of a metal cation from the aqueous phase by a host compound, in order to preserve electrical neutrality. Thus, a measure of the ability of a host to bind a given metal ion can be obtained through simple spectrophotometric measurements. The use of oxonol dyes in place of picrate salts offers several advantages when applied as a rapid screening technique.[4] The dyes are straightforward to synthesize for a range of alkali, alkaline-earth and transition metals, and are far safer to handle than the

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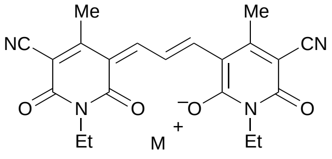
‡ Infrared spectroscopy reveals that in acetonitrile solution the amide carbonyl stretching frequency of compound **9** (1604 cm^{-1}) is subject to only a small change on the addition of 1 equivalent of either lithium (1602 cm^{-1}) or sodium (1610 cm^{-1}) perchlorate. It could perhaps be argued that the change in the sodium case, although small, is consistent with a slight strengthening of the C–N bond resulting from metal-ion binding within the crown cavity.

Table 3 Percentage extraction abilities for metallocene crowns with a range of metal-ion oxonol dyes

	Metal-ion oxonol dye						
Crown	Li$^+$	Na$^+$	K$^+$	NH$_4^+$	Ag$^+$	Mg^{2+}	Ca^{2+}
9	25	32	30	44	40	0	0
15	99	97	99	99	100	54	48
10	20	19	18	34	27	0	0
16	99	98	97	99	100	58	55
1	97	95	100	97	68	35	28



17, M$^+$ = Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Ag$^+$, Ba^{2+}, Ca^{2+}

corresponding picrates. As photographic dyes they have very high absorption coefficients (≈ 10^5 dm^3 mol^{-1} cm^{-1} in water and organic solvents) thus facilitating simple spectrophotometric assays. Full experimental detail concerning the extraction technique is given in the Experimental section. Percentage extractions for a range of oxonol dyes **17** by metallocene crowns **9**, **10**, **15**, **16** and, for comparative purposes, bis(crown) **1** are given in Table 3.

Unsurprisingly, the amino-linked crowns **15** and **16** are far more effective complexing agents than are their amido-linked analogues **9** and **10**. The amide link would be expected both to limit the flexibility of the crown, and reduce the electron density associated with the nitrogen donor atom. Tertiary amine crowns **15** and **16** effect near total transfer of all the monovalent cations studied and transfer approximately 50% of the divalent cations, an extraction efficiency comparable with that of ferrocene bis(crown) **1**. Silver ion binding is far stronger with these simple crowns, a direct consequence of the presence in these structures of tertiary amine donor sites as opposed to the amido nitrogen centres present in **1**.

It is interesting that the extraction behaviour of compounds **15** and **16** is virtually identical throughout the range of metal ions studied. Of their amido-linked analogues **9** and **10**, the ferrocene derivative **9** consistently extracts a slightly higher percentage of metal ion than does the ruthenocene analogue **10**. This may result from greater communication of the more electron-rich nature of ferrocene[9] through the conjugated amide link to the nitrogen donor atom, thus increasing the binding strength through increased electrostatic interactions.

^{13}C NMR spectroscopic studies of alkali-cation binding

The binding of a metal ion by a host molecule is accompanied by conformational and electronic changes which, in turn, are reflected by variations in the ^{1}H and ^{13}C NMR chemical shifts of those centres close to the site of complexation.[16] Since the ^{1}H NMR spectra of cyclic polyethers are found to be complex and rather difficult to interpret it has proved more convenient to follow the binding behaviour of our systems using ^{13}C NMR spectra. The ^{13}C chemical shifts are known to be sensitive to conformational changes but relatively less sensitive to solvent effects, and offer the possibility of using distortionless enhancement of polarisation transfer (DEPT) experiments to aid in assignment.[17,18]

Having identified tertiary amine crowns **15** and **16** as the more effective ionophores, we performed NMR binding titrations with Na$^+$ ions by monitoring variations in the ^{13}C NMR chemical shifts in the presence of varying quantities of NaClO$_4$ in CD$_3$CN solutions of the crowns. The chemical shifts and peak assignments are given in Table 4. The data for both crowns are entirely consistent with the formation of 1:1 stoichiometry complexes; no further changes are observed once a 1:1 ratio of crown:Na$^+$ has been reached. Considerable changes in the chemical shifts for all the methylene resonances of the crown are observed together with changes in the resonances associated with the carbons of the substituted metallocene ring. However, the signal arising from the unsubstituted cyclopentadienyl ring remains essentially unaffected (±0.05 ppm) throughout the titration experiment suggesting that it is unperturbed by the sodium-ion co-ordination process. This observation suggests that this ring is not included in whatever conformational processes occur upon the addition of sodium ions, whilst the substituted cyclopentadienyl ring and the crown ring operate in concert to effect binding. A possible explanation accounting for these observations is outlined in schematic form (Fig. 1).

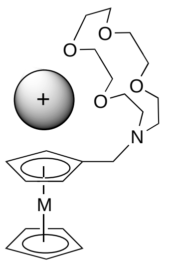
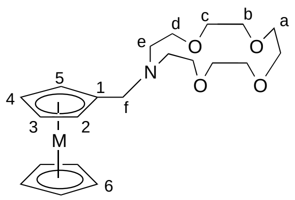


Fig. 1 Proposed mode of cation complexation in compounds **15**·Na$^+$ and **16**·Na$^+$

Although the term π complex is normally associated with transition-metal species, like ferrocene itself, many compounds that feature π-facial complexation of a ligand to a main-group element are now known.[19] There are examples of cation π interactions within structures containing both π-electron-rich systems and polyether chains,[20] benzene rings are known to be effective donors for metal cations in a variety of complexes,[21–26] and potassium-ion transport has been observed in biological systems through channels lined with aromatic residues by a mechanism thought to involve cation π interactions.[27] Of particular relevance to the present discussion is the crystal structure of [Li(12-crown-4)]$^+$[η^5-C$_5$H$_5$]$^-$ (12-crown-4 = 1,4,7,10-tetraoxacyclododecane) which has a pseudo-sandwich arrangement with the Li$^+$ ion bound on one face by the oxygen atoms of the crown ether, and on the other by the π face of the aromatic cyclopentadienyl anion.[28] The simple hosts **15** and **16** are the first examples of metallocene-derived crowns which possess the structural flexibility required to achieve such a dual binding interaction. The requirement of coplanarity between the cyclopentadienyl ring and the amide links present in the majority of reported systems ensures that such a binding mode is structurally impossible.

The only available data[8] with which to compare our studies is that for metal-ion binding by the ferrocenylcryptand **4**, the accurate spectral assignment of which was reported by Plenio *et al.*[1] The ^{13}C NMR binding data presented for cryptand **4** were used to demonstrate the high level of symmetry present in both the free cryptand and its metal-ion complexes. The results suggest that this host presents a single well defined binding cavity. Closer inspection of those data reveals similar trends in the changes of the OCH$_2$ resonances (1–1.5 ppm upfield) on metal-ion binding in comparison with those observed with **15** and **16** (1–2.5 ppm upfield). The diazacrown unit of **4** is known to be rather constrained and the larger shifts observed with the present systems are likely to be a reflection of a better binding fit between the cation and crown. There are also notable differences in the behaviour of the ferrocenyl carbon resonances. The quaternary carbons of **4** shift upfield by ≈1.3 ppm in the **4**·Na$^+$ complex whilst larger upfield shifts of ≈1.9 and 2.3 ppm are observed for **15**·Na$^+$ and **16**·Na$^+$. A more dramatic difference may be noted in the shifts of the resonances of the *o*-carbons

Table 4 Carbon-13 NMR shifts (δ) of compounds **15** and **16** with added sodium perchlorate



Compound **15**

Ratio*	C^1	C^b	$C^{2,5}$	C^a	C^c	C^d	C^6	$C^{3,4}$	C^f	C^e
0.00 : 1	82.83	71.45	71.13	70.87	70.72	70.27	69.45	68.81	56.47	54.71
0.25 : 1	82.12	71.06	71.43	70.64	70.56	69.52	69.51	68.96	54.78	54.32
0.50 : 1	81.54	70.87	71.56	70.04	70.23	68.43	69.48	69.01	53.87	53.06
1.00 : 1	80.90	69.62	71.80	69.62	69.03	67.59	69.54	69.25	52.65	53.06
1.50 : 1	80.93	69.64	71.79	69.65	69.10	67.59	69.53	69.20	52.66	53.00

Compound **16**

Ratio*	C^1	$C^{2,5}$	C^6	$C^{3,4}$	C^a	C^b	C^c	C^d	C^f	C^e
0.00 : 1	83.20	73.33	71.50	71.50	71.01	70.92	70.79	70.07	56.22	54.62
0.25 : 1	82.65	73.44	71.52	71.52	71.08	70.56	70.56	69.47	55.53	54.29
0.50 : 1	81.54	73.62	71.55	71.22	71.52	70.25	69.99	68.65	53.55	53.82
1.00 : 1	80.98	73.82	71.62	71.44	69.76	69.76	69.15	67.43	53.11	53.11
1.50 : 1	80.90	73.87	71.55	71.28	69.56	69.56	69.01	67.59	52.63	53.04
2.00 : 1	80.91	73.88	71.55	71.30	69.57	69.57	69.02	67.57	52.63	52.04

* Molar ratio of $NaClO_4$ to crown.

($C^{2,5}$). For the **4**·Na^+ complex an *upfield* shift of 2.3 ppm is observed; the **15**·Na^+ and **16**·Na^+ complexes display *downfield* shifts of 0.6–0.7 ppm.

The ^{13}C NMR spectral changes observed in the conversion of compound **11** into the quaternary ammonium salt **13** provide a model for the effect of the introduction of a positive charge at the nitrogen centre of **15** and **16**; this effect may be considered similar in nature, but far greater in magnitude, to the participation of the nitrogen centre in cation binding. In the conversion of **11** into **13** the $C_5H_4CH_2$ resonance shifts around 8 ppm *downfield*. This is at variance with the situation observed for the complexes **15**·Na^+ and **16**·Na^+ where *upfield* shifts of the same resonance by 3.5–4 ppm are recorded. Such a contrast indicates that it is unlikely that the cation-induced changes in the spectra of **15** and **16** are the result of an inductive effect arising from the binding of a cation in the crown ring.§ To rationalise the difference in behaviour of the relative $C_5H_4CH_2$ shifts it is proposed that the nitrogen lone pairs of **15** or **16** do not directly participate in the binding of the metal cation. Corey–Pauling–Koltun (CPK) models support this view by demonstrating that our proposed binding conformation for **15**·Na^+ (Fig. 1) requires the nitrogen lone pair to point almost directly away from the binding cavity.

Whilst the results of a ^{13}C NMR titration of compound **16** with $KClO_4$ initially seemed inconsistent with the effects observed in the Na^+ case, more detailed analysis indicated the presence of a rather delicate binding equilibrium. Unlike the Na^+ titration, at less than 1 equivalent of added cation no appreciable shifts of any of the ferrocenyl resonances are apparent whereas the shifts for the methylene carbons are broadly consistent with those reported for the potassium complex of **4**. These observations may indicate that at crown : K^+ ratios of <1 : 1 co-ordination is dominated by 2 : 1 sandwich host–guest complexation (Fig. 2). Behaviour of this kind has previously been noted with other metallocene monocrowns, especially those derived from 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane),[29] a crown ether which has a well documented ability to form 2 : 1 sandwich type complexes with potassium salts. No appreciable shifts of the ferrocenyl resonances would be expected for a complex of this type since, unlike cryptand **4** where the binding site is ‘tied’ to both ferrocene rings, no conformational reorganisation involving the ferrocene unit is required. On the addition of an excess of $KClO_4$ (crown : K^+ >1 : 1) the shifts become consistent with the model proposed for **15**·K^+, the host simply switching binding modes in response to the increased concentration of K^+ ions present. The proposed binding equilibrium is presented schematically in Fig. 2.

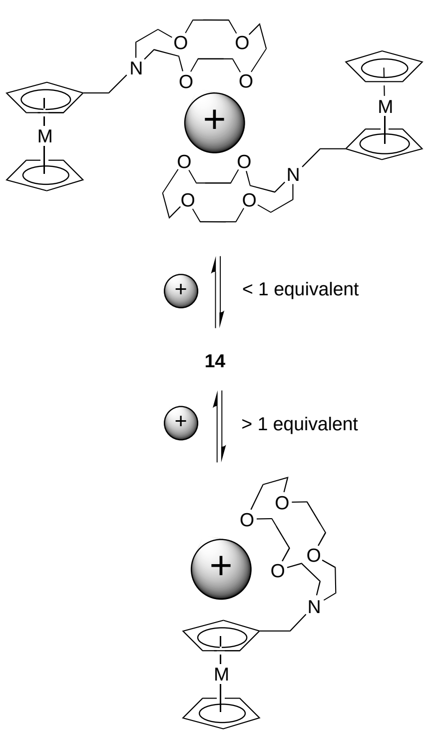


Fig. 2 Equilibria for the binding of K^+ by compound **15**

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§ The UV/VIS spectral investigation of compound **15**, its cation complexes and the model compounds **11** and **13** was undertaken in acetonitrile solution. In the case of the model compounds a hypsochromic shift of around 7 nm was observed in the conversion of **11** (λ_{max} = 404 ± 1 nm) into **13** (398 ± 1 nm). In contrast, no cation-induced shifts were observed upon the addition of lithium, sodium or potassium perchlorate to solutions of ferrocene crown **15** (λ_{max} = 404 ± 1 nm in all cases).

Table 5 Electrochemical oxidation potentials (mV) for compound **15** with added $NaPF_6$ or KPF_6

	Oxidation potential (mV)	
Molar ratio*	E_{Na^+}	E_{K^+}
0.0 : 1	480	480
0.5 : 1	520	510
1.0 : 1	560	530

* Molar ratio MPF_6 to crown.

Table 6 Electrochemical oxidation potentials (mV) for compound **16** with added $NaPF_6$ or KPF_6

	Oxidation potential (mV)			
	Na^+		K^+	
Molar ratio[a]	E_1	$E_{1'}$	E_1	$E_{1'}$
0.00 : 1	420	*b*	420	*b*
0.25 : 1	420	*b*	420	490
0.50 : 1	420	520	*b*	490
0.75 : 1	420	520	*b*	490
1.00 : 1	*b*	520	*b*	490

$E_2 = 620$ mV in each case. [a] Molar ratio MPF_6 to crown. [b] Not observed.

Cyclic voltammetry

The electrochemical response of metallocenylcrowns and cryptands to the presence of a guest species has always been the primary motivation behind their design and synthesis.[5] The groups of Saji[30] and Hall[31] were the first to report a correlation between the shift of the ferrocene–ferrocenium redox couple and the charge–radius ratio of the guest cation. More recently Plenio and co-workers[32,33] have demonstrated a relation between the spatial separation of the ferrocenyl iron centre from the bound guest and the redox potential of the complex. Such analysis holds for redox switching of sodium ion binding[32] and protonation of a number of ferrocene amines, crowns and cryptands.[33]

Cyclic voltammetric analysis (see Experimental section) of compound **15** in acetonitrile reveals the expected one-electron reversible oxidation process at 480 mV. The changes observed on the addition of increasing amounts of $NaPF_6$ and KPF_6 are shown in Table 5. The addition of stoichiometric equivalents of these salts to **15** resulted in anodic shifts (ΔE) of the ferrocene–ferrocenium redox couple of 80 and 50 mV, respectively. These shifts appear rather small when compared with those reported for ferrocenylcryptand **4** ($\Delta E_{Na^+} = 188$, $\Delta E_{K^+} = 124$ mV),[8] where the cation is of necessity held in close proximity to the iron centre, but are similar to the electrochemical responses reported for the ferrocenylbis(crowns) **1** ($\Delta E_{Na^+} = 70$ mV)[7] and **2** ($\Delta E_{Na^+} = 90$, $\Delta E_{K^+} = 60$ mV).[3] The responses obtained for **15** indicate that there is significant cation redox interaction and that, if our proposed binding model is valid under the conditions of the electrochemical studies, then metal ion co-ordination to the π face of the metallocene provides effective communication of the binding event to the redox centre.

Ruthenocene derivatives are known to undergo two distinct, irreversible one-electron oxidation processes.[34] Such a lack of reversibility has ensured that no electrochemical investigation of cation binding by a ruthenocene-derived crown has been reported. Accordingly, the electrochemical behaviour of compound **16** in the presence of varying amounts of $NaPF_6$ and KPF_6 has been studied and the results are summarised in Table 6. The first and second oxidation potentials of the free crown are represented by E_1 and E_2, the first oxidation potential of the cation complex being denoted by $E_{1'}$. As the ratio of cation to crown is increased the oxidation potential of the free crown gradually gives way to that of the complex. The measured shifts ($\Delta E_{Na^+} = 100$, $\Delta E_{K^+} = 80$ mV) are comparable with those obtained for the ferrocene analogue **15**. The invariable value of the second oxidation potential (E_2) may be rationalised by recognising that the first oxidation process generates a formally charged metallocene centre $[Ru^{III}(C_5H_5)_2]^+$, and, paralleling the behaviour reported for ferrocene systems,[35,36] the positively charged metallocene derivative then ejects the bound cation as a result of unfavourable electrostatic interaction. Consequently, since the cation is no longer associated with the host, the value of the second oxidation potential remains constant throughout the experiment.

Conclusion

The work described in this paper allows two observations to be made concerning the properties of simple metallocene azacrown ethers: (*i*) the presence of an amino-, rather than an amido-, link between the metallocene and azacrown ether greatly enhances cation binding ability, and (*ii*) in solution, simple amino-linked metallocene–azacrown ethers may have available a binding mode involving a stabilising π interaction between a guest cation and the π system of the metallocene. Few previously reported metallocene crowns possess the conformational or geometrical freedom to adopt such a co-ordination mode.

The possibility of π participation in cation binding by compounds **15** and **16** is an intriguing addition to the known modes of cation complexation adopted by ferrocene crowns and cryptands. The original ferrocene-based cryptand **3** is known to bind cations both internally, within the crown residues, and externally, *via* two *cis*-oriented amide-carbonyl groups.[6] Both situations are also observed with ferrocene bis(crowns) such as **2**.[7] Gokel and co-workers[8] have shown that the amino-linked cryptand **4** has only one well defined binding cavity, and in addition may allow direct d-orbital interaction between the ferrocenyl iron centre and a guest cation such as silver. The present work suggests that in sufficiently flexible systems the π system of the metallocene may also act as a donor group for a bound cation, though in the absence of solid-state structural data it is not possible to provide absolute proof for this hypothesis, or to discount alternative interpretations. Further investigation of the nature and importance of this interaction in these and related systems is currently in progress.[37]

Experimental

General

Column chromatography was performed on flash silica (Rhône-Poulenc, Sorbsil C60-H, 40–60 mesh) or alumina (Fluka, Type 507 C Neutral, Brockmann Grade 1, 100–125 mesh). All melting points were determined in open capillary tubes using a Gallenhamp Electrothermal melting point apparatus and are uncorrected. Combustion analyses were performed by Medac Ltd., Brunel University. Fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical normal geometry double-focusing mass spectrometer, UV/VIS spectral measurements on Perkin-Elmer 550S and 551S spectrophotometers, IR spectra using a 1600 Series Perkin-Elmer Fourier-transform spectrophotometer and NMR spectra on JEOL 270 MHz and Bruker 360 MHz spectrophotometers. Cyclic voltammetric electrochemical measurements were made using unstirred solutions of the compounds in dry acetonitrile (5 mM) containing $NBu^n{}_4PF_6$ (30 mM) as the supporting electrolyte using a custom-built potentiostat with platinum working and auxiliary electrodes, and a standard calomel reference electrode.

Preparations

1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylcarbonylferrocene 9. A suspension of ferrocenecarboxylic acid[38] **5** (500 mg, 2.17 mmol) in dry CH_2Cl_2 (15 cm^3) containing dry dmf (2 drops) was treated under N_2, with stirring, with a solution of oxalyl chloride (2.21 g, 1.52 cm^3, 17.4 mmol) in dry CH_2Cl_2 (15 cm^3) and the resulting mixture stirred overnight. The solvent was then removed under reduced pressure and the residue recrystallised from dry hexane to yield dark red plates of chlorocarbonylferrocene **7** (520 mg, 95%). A solution of aza-15-crown-5[39,40] (132 mg, 0.6 mmol) and dry triethylamine (66 mg, 0.09 cm^3, 0.66 mmol) in dry benzene was treated dropwise with a solution of chlorocarbonylferrocene (150 mg, 0.6 mmol) in dry benzene (10 cm^3) over 10 min. The resulting mixture was stirred for a further hour and then filtered and the solvent removed under reduced pressure. The residual oil was purified by column chromatography (neutral Al_2O_3; CH_2Cl_2 then 2% MeOH in CH_2Cl_2; $R_f = 0.60$, 1% MeOH in CH_2Cl_2) to afford an orange oil (254 mg, 98%); $\tilde{\nu}_{max}/cm^{-1}$ ($CDCl_3$) 2900m, 1603s, 1474s, 1410m, 1381m, 1295w, 1264w, 1216w, 1127s and 1098s; δ_C(75 MHz, $CDCl_3$) 170.80 (C=O), 77.72 (C^1), 71.77 (CH_2O), 70.72 ($C^{2,5}$), 70.34, 70.24 ($C^{3,4}$ and OCH_2), 69.79 (C_5H_5), 50.80, 50.08 (NCH_2); δ_H(270 MHz, $CDCl_3$) 4.67 (2 H, s, $H^{2,5}$), 4.29 (2 H, s, $H^{3,4}$), 4.21 (5 H, s, C_5H_5), 3.80–3.60 (20 H, m, CH_2); FAB accurate mass: *m/z* 432.1432 (Found), $C_{21}H_{30}FeNO_5$ ($[M + H]^+$) requires 432.1473.

1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylcarbonylruthenocene 10. Treatment of a suspension of ruthenocenecarboxylic acid[41] **6** (500 mg, 1.82 mol) in dry CH_2Cl_2 (15 cm^3) containing dry dmf (2 drops) with a solution of oxalyl chloride (1.84 g, 1.27 cm^3, 14.5 mmol) in dry CH_2Cl_2 (15 cm^3) and stirring overnight under N_2 afforded the acid chloride derivative **8** after solvent evaporation and recrystallisation from hexane (482 mg, 90%). A solution of aza-15-crown-5 (187 mg, 0.85 mmol) and dry triethylamine (95 mg, 0.13 cm^3, 0.94 mmol) in dry benzene (10 cm^3) was treated dropwise with a solution of chlorocarbonyl ruthenocene (250 mg, 0.85 mmol) in dry benzene (10 cm^3) over 10 min and then stirred for a further hour. The mixture was then filtered, evaporated under reduced pressure and purified by column chromatography (neutral Al_2O_3; CH_2Cl_2 then 2% MeOH in CH_2Cl_2; $R_f = 0.65$, 1% MeOH in CH_2Cl_2) to afford a pale yellow oil (390 mg, 96%); $\tilde{\nu}_{max}/cm^{-1}$ ($CDCl_3$) 2868m, 1600s, 1477s, 1410m, 1380m, 1354m, 1293m, 1250w, 1127s and 1100s; δ_C(75 MHz, $CDCl_3$) 169.60 (C=O), 81.40 (C^1), 72.85 ($C^{2,5}$), 72.00 ($C^{3,4}$), 71.79 (C_5H_5), 70.31, 70.21 (CH_2O), 51.26, 49.90 (CH_2N); δ_H(270 MHz, $CDCl_3$) 4.99 (2 H, apparent t, $J = 2$, $H^{2,5}$), 4.62 (2 H, apparent t, $J = 2$ Hz, $H^{3,4}$), 4.58 (5 H, s, C_5H_5), 3.74 (4 H, br s, NCH_2), 3.53 and 3.51 (16 H, 2 × s, OCH_2); FAB accurate mass: *m/z* 478.1129 (Found), $C_{21}H_{30}NO_5Ru$ ($[M + H]^+$) requires 478.1167.

Trimethylammoniomethylruthenocene iodide 14. A mixture of ruthenocene[42] (2.00 g, 8.66 mmol), *N,N,N′,N′*-tetramethyldiaminomethane (1.49 g, 2.00 cm^3, 14.0 mmol), orthophosphoric acid (1.5 cm^3 of a 85% aqueous solution) and acetic acid (25 cm^3) was heated at 100 °C for 5 h with vigorous stirring under a N_2 atmosphere. The reaction was allowed to cool and diluted with water (50 cm^3); extraction with diethyl ether (2 × 50 cm^3) recovered unchanged ruthenocene (1.14 g, 57%). The aqueous extracts were cooled in ice and made alkaline with the addition of NaOH pellets (20.0 g, 0.5 mol). Extraction with diethyl ether (2 × 50 cm^3) afforded a small volume of a pale yellow oil. This crude oil was dissolved in methanol (25 cm^3), methyl iodide (3.70 g, 1.62 cm^3, 0.026 mol) added slowly and the resulting solution subsequently refluxed for 30 min before being cooled to room temperature and poured dropwise into stirred diethyl ether (100 cm^3). The precipitated pale yellow solid was collected at the pump, washed with diethyl ether (2 × 50 cm^3) and dried *in vacuo* (1.41 g, 38%), m.p. 155–170 °C (decomp.) (Found: C, 38.77; H, 4.61; N, 3.26. $C_{14}H_{20}INRu$ requires C, 38.98; H, 4.68; N, 3.22%); $\tilde{\nu}_{max}/cm^{-1}$ ($CDCl_3$) 2974w, 2888w, 2739w, 1814w, 1787w, 1477s, 1461s, 1381s, 1295w, 1247w, 1210w, 1167w, 1092m, 1044m and 980w; δ_C[75 MHz, $(CD_3)_2SO$] 76.83 (C^1), 74.07 ($C^{2,5}$), 72.23 ($C^{3,4}$), 71.43 (C_5H_5), 65.00 (CH_2) and 44.34 (CH_3); δ_H(270 MHz, $CDCl_3$) 4.89 (2 H, d, $J = 2$, $H^{2,5}$), 4.70 (2 H, d, $J = 2$ Hz, $H^{3,4}$), 4.66 (5 H, s, C_5H_5), 4.54 (2 H, s, CH_2) and 3.36 (9 H, s, CH_3); FAB mass spectrum: *m/z* 430 (M^+, 100%).

***N*-Ferrocenylmethyl-1,4,7,10-tetraoxa-13-azacyclopentadecane 15.** A solution of trimethylammoniomethylferrocene iodide[43] **13** (1.03 g, 2.68 mmol) in dry acetonitrile (40 cm^3) was added dropwise over 1 h to a refluxing solution of aza-15-crown-5 (420 mg, 1.92 mmol) in dry acetonitrile (40 cm^3) containing anhydrous potassium carbonate (874 mg, 6.32 mmol) and the mixture refluxed for 6 h. After cooling the mixture was filtered and the solids washed with hot acetonitrile (2 × 20 cm^3). The solvent was removed from the organic extracts under reduced pressure, the residue dissolved in CH_2Cl_2 (50 cm^3) and washed with water (2 × 100 cm^3). The organic extracts were then dried over $MgSO_4$ and evaporated to yield an orange oil which was purified by column chromatography (neutral Al_2O_3; 2% MeOH in CH_2Cl_2; $R_f = 0.40$, 2% MeOH in CH_2Cl_2) to afford an orange oil (640 mg, 80%); $\tilde{\nu}/cm^{-1}$ ($CDCl_3$) 3097w, 2875s, 1656m, 1561w, 1468s, 1381s, 1357m, 1254m, 1264m, 1126vs, 1042m and 1001m; δ_C(75 MHz, $CDCl_3$) 71.61 ($C^{2,5}$), 70.12 ($C^{3,4}$), 69.97, 69.69, 69.51, 69.34 (OCH_2), 69.22 (C_5H_5), 64.70 (OCH_2), 55.50, 53.60 (CH_2N) and 52.82 ($C_5H_4\mathit{C}H_2N$); δ_H(270 MHz, $CDCl_3$) 4.53 (2 H, s, $H^{2,5}$), 4.50 (2 H, s, $C_5H_4C\mathit{H}_2N$), 4.29 (2 H, s, $H^{3,4}$), 4.25 (5 H, s, C_5H_5), 3.68 (16 H, m, OCH_2) and 3.49 (4 H, br s, NCH_2); FAB accurate mass: *m/z* 418.1673 (Found), $C_{21}H_{32}FeNO_4$ ($[M + H]^+$) requires 418.1681.

***N*-Ruthenocenylmethyl-1,4,7,10-tetraoxa-13-azacyclopentadecane 16.** Following the procedure given above for the ferrocene analogue, reaction of aza-15-crown-5 (330 mg, 1.50 mmol) with compound **14** (712 mg, 1.66 mmol) in dry acetonitrile (80 cm^3) containing anhydrous potassium carbonate (684 mg, 4.95 mmol) afforded the crude crown. Column chromatography (neutral Al_2O_3; 2% MeOH in CH_2Cl_2; $R_f = 0.42$, 2% MeOH in CH_2Cl_2) provided the pure crown derivative (580 mg, 83%); $\tilde{\nu}_{max}/cm^{-1}$ ($CDCl_3$) 2900s, 1640w, 1561w, 1468s, 1381s, 1295w, 1248w, 1216w and 1098vs; δ_C(75 MHz, $CDCl_3$) 77.40 (C^1), 72.58 ($C^{2,5}$), 71.07 ($C^{3,4}$), 70.72 (C_5H_5), 70.52, 70.40, 70.26, 69.70 (OCH_2), 55.78 ($C_5H_4\mathit{C}H_2N$) and 53.60 (NCH_2); δ_H(270 MHz, $CDCl_3$) 4.59 (2 H, s, $H^{2,5}$), 4.50 (5 H, s, C_5H_5), 4.48 (2 H, s, $H^{3,4}$), 3.64 (16 H, br s, OCH_2), 3.40 (2 H, s, $C_5H_4C\mathit{H}_2N$) and 2.80 (4 H, t, $J = 6$ Hz, NCH_2); FAB accurate mass: *m/z* 464.1339 (Found), $C_{21}H_{32}NO_4Ru$ ($[M + H]^+$) requires 464.1375.

Calculation of amide bond-rotation barriers from ^{13}C NMR spectra

The Gutowsky[44] and Eyring[45] equations may be combined to yield equation (1) where $k_C = \Delta\nu(\pi/\sqrt{2})$. Activation energies

$$\Delta G^{\ddagger} = (19.148)T_c(10.319 - \log_{10} k_c + \log_{10} T_c) \quad (1)$$

($\Delta G^{\ddagger}$) may thus be calculated from knowledge of the coalescence temperature (T_c) of the exchange process and the frequency separation ($\Delta\nu$) of the individual resonances in the *frozen* condition. The quoted errors reflect the inherent difficulty of accurately determining both the coalescence temperature (a change of 1 K results in a shift of around 0.2 kJ mol^{-1}), and the coalescence point (computational lineshape spectral analysis would be required accurately to determine this parameter).

Extraction experiments with oxonol dye salts[4]

Oxonol dye salts were prepared according to literature methods[46] and recrystallised to constant absorption coefficient prior to use in the extraction experiments. Typically two to three recrystallisations of each dye salt were required. Absorption coefficients (ε_{max}) for each dye salt in water were determined in the concentration range 10^{-6} to 10^{-4} M of standard solutions prepared by serial dilutions of a 5×10^{-4} M solution of the dye in deionised water. The average value over this range was used in all calculations. Equal volumes (10 cm^3) of equimolar (1.5×10^{-5} M) solutions of oxonol dye (in water) and a CH_2Cl_2 solution of crown were shaken mechanically at ambient temperature for 10 min in sealed vessels. Each two-phase system was then allowed to separate for 10 min. Taking care to avoid solvent evaporation, aliquots of the aqueous layer were then removed and the absorbance of the sample at 589 nm determined; each measurement was repeated five times. The percentage of oxonol dye remaining in the aqueous layer was given by $(A/A_0) \times 100$, where A_0 is the absorbance of the aqueous layer prior to extraction and A that following extraction. Each determination was repeated five times.

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