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Preliminary communication

Redox responsive crown ethers containing a direct link between the ferrocene redox-active centre and benzo crown ether. Crystal structure of a ferrocene benzo-15-crown-5 sodium complex

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Abstract

The binding of Na^+, K^+ and Mg^{2+} to benzo-15-crown-5 and aza-15-crown-5 directly-linked ferrocenes results in shifts of the ferrocene oxidation wave to more positive potentials. The magnitude of these anodic shifts is related to the charge/radius ratio of the cationic guest. The results of an X-ray diffraction study of the structure of a ferrocene benzo-15-crown-5 sodium complex are also reported.

There is considerable current interest in the synthesis of redox responsive macrocycles that contain redox-active functions such as quinone [1], nitrobenzene [2] and metallocene [3,4] moieties in close proximity to a cation binding site. Interest in these molecules stems from the idea of studying mutual interactions (e.g. electron transfer) between the redox-active centre and a closely bound metal cation. If the binding site can be designed to be selective towards a certain cationic guest then the resulting host molecules may serve as components of new chemical sensory devices [5].

We report here the synthesis, coordination and electrochemistry of the first examples **1** and **2** of a class of compound in which the ferrocene subunit is directly linked to a benzo crown ether moiety, including the crystal structure of $[(\mathbf{1})Na]PF_6$. We also present evidence that metal cation binding at the crown ether moieties perturbs the redox potential of the ferrocene/ferricinium couple.

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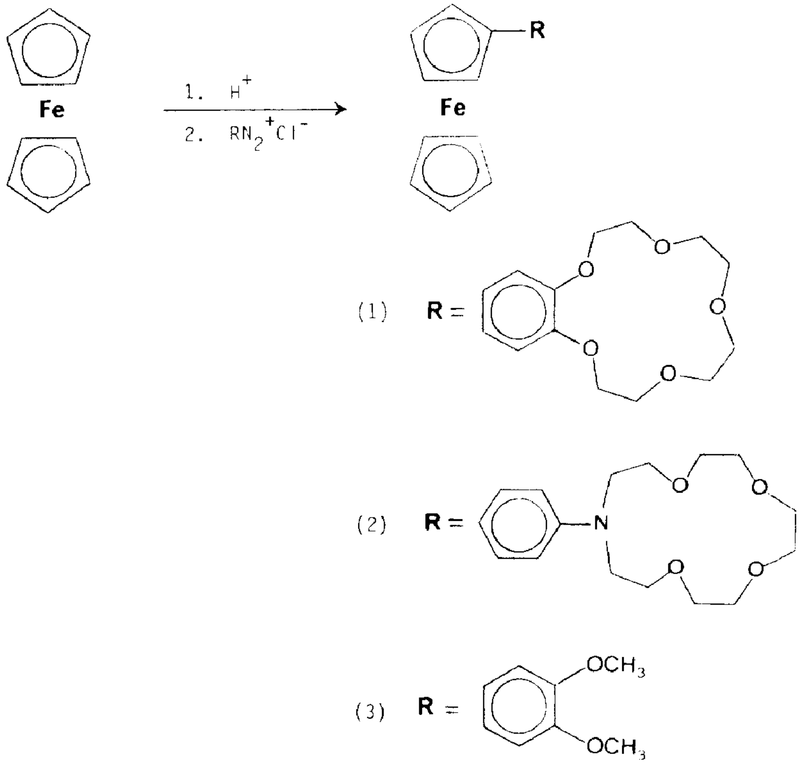

Scheme 1.

Compounds **1**, **2** and **3** were prepared by the method Weinmayr [6] used for the synthesis of arylferrocenes. Dissolving ferrocene in concentrated sulphuric acid initially produces the ferricinium ion, which on treatment with the diazonium salt of the appropriate aromatic amine [7,8], gives 30, 25 and 20% yields of **1**, **2** and **3**, respectively, Scheme 1. The structure of these new air stable compounds were established by elemental analysis, mass spectrometry, and ^{1}H NMR spectroscopy.

Refluxing aqueous methanolic solutions of sodium or potassium hexafluorophosphate led to the successful isolation of the respective complexes [(**1**)Na]PF$_6$, [(**1**)$_2$K]PF$_6$, [(**2**)Na]PF$_6$ and [(**2**)$_2$K]PF$_6$, which were also detected by FAB mass spectrometry.

Slow evaporation of an aqueous methanolic solution of [(**1**)Na]PF$_6$ led to the isolation of orange crystallographic-quality crystals *. The structure consists of discrete molecules of [(**1**)Na]PF$_6$ shown in Figs. 1(a) and 1(b). The sodium cation is

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* Crystal data ** for [(**1**)Na]PF$_6$, [C$_{24}$H$_{28}$F$_6$FeNaO$_5$P], $M = 620.0$, monoclinic, a [C$_{24}$H$_{28}$F$_6$FeNaO$_5$P] 18.511(15), b 7.666(8), c 38.758(25) Å, β 103.0(1), U 5359.0 Å^3, $F(000)$ 2544, d_m 1.53 g cm^{-3}, d_c 1.56 g cm^{-3}, $Z = 8$, Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α) 7.47 cm^{-1}, Spacegroup $C2/c$. 5413 independent reflections above background ($I > 2\sigma(I)$) were measured on a diffractometer. The structure was determined by heavy atom methods and refined by full matrix least squares (Fe, Na, P, F, C, O anisotropic, H isotropic in fixed positions) to $R = 0.079$ ($W_w = 0.085$).

** The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

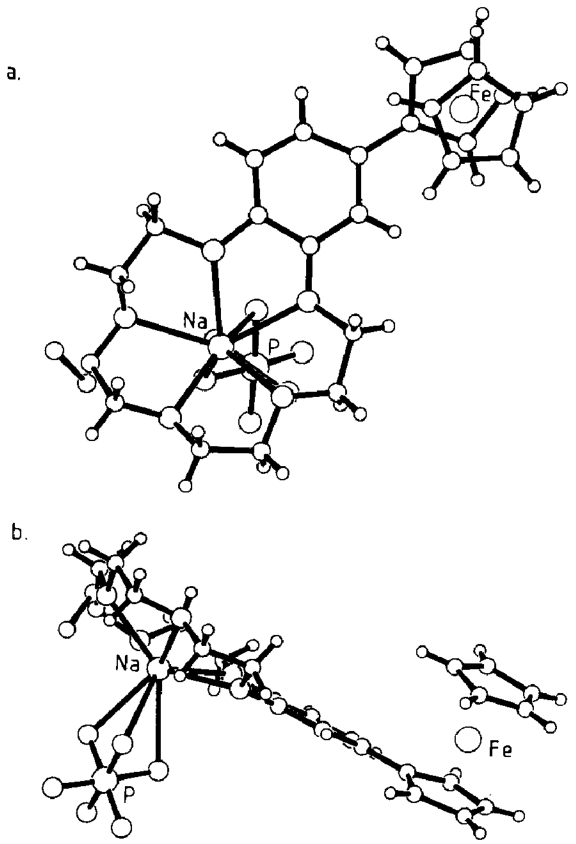

Fig. 1. Crystal structure of [(**1**)Na]PF_6 showing: (a) the Na^+ bound to all five oxygens of the benzo-crown ether; (b) the Na^+ lying above the 15-crown-5 ligand coordinated to PF_6^-.

bound to all five oxygens of the benzo-crown ether with Na–O distances ranging from 2.38(1) to 2.48(1) Å. (Fig. 1(a)). The sodium ion lies above the 15-crown-5 ligand (0.88 Å above a least squares plane of the five oxygen atoms; maximum deviation 0.32 Å). On the other side of the sodium ion are three fluorine atoms of a PF_6^- anion, with dimensions Na–F 2.54(2), 2.69(1), 2.89(3) Å. (Fig. 1(b)).

Table 1

Electrochemical data

Compound	**1**	**2**	**3**
E_f (V) [a]	+0.54	+0.58	+0.55
ΔE_p (mV) [b]	80	80	80
$\Delta E(Na^+)$ (mV) [c]	60	90	<10
$\Delta E(K^+)$ (mV) [c]	20	40	<10
$\Delta E(Mg^{2+})$ (mV) [c]	70	110	<10

[a] Obtained in MeCN solution containing 0.2 *M* $[Bu_4N]BF_4$ as supporting electrolyte. Solutions were ca. 2×10^{-3} *M* in complex and potentials were determined with reference to SCE. [b] Separation between anodic and cathodic peak potentials of cyclic voltammograms, values for ferrocene under the same conditions ranged from 75–85 mV. [c] Shift in oxidation potential produced by presence of metal cation (4 equiv.) added as their hexafluorophosphate salts for sodium and potassium and thiocyanate salt for magnesium.

The electrochemistry of **1**, **2** and a model compound **3** was investigated in acetonitrile solution by cyclic voltammetry with $[Bu_4N]BF_4$ as the supporting electrolyte. Cyclic voltammograms were also recorded after addition of Na^+, K^+, Mg^{2+} cations to the electrochemical solutions, and the results obtained are presented in Table 1.

Only in the case of **1** and **2** are significant anodic shifts produced with the three cationic guests. It is noteworthy that the magnitude of these shifts is related to the charge/radius ratio of the cationic guest, magnesium causing the largest value and potassium the smallest. These results suggest that the polarising power of the cation is of great importance in determining the magnitude of the anodic shift in E_f produced by cationic binding.

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References

1 L. Echegoyen, D.A. Gustowski, V.J. Gatto and G.W. Gokel. J. Chem. Soc. Chem. Commun., (1986) 220.
2 D.A. Gustowski, L. Echegoyen, D.M. Goli, A. Kaifer, R.A. Schultz and G.W. Gokel. J. Am. Chem. Soc., 106 (1984) 1633.
3 P.D. Beer, J. Chem. Soc. Chem. Commun., (1985) 1115.
4 T. Saji, Chem. Lett., (1986) 275.
5 P.D. Beer, Aldrichimica Acta, in press.
6 V. Weinmayr, J. Am. Chem. Soc., 77 (1955) 3012.
7 R. Ungaro, B. El Haj and J. Smid, J. Am. Chem. Soc., 98 (1977) 5198.
8 J.P. Dix and F. Vögtle, Chem. Ber., 113 (1980) 457.