Selective Electrochemical Recognition of the Potassium Guest Cation in the Presence of Sodium and Magnesium Ions by a New Ferrocenyl Ionophore

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The new ferrocenyl ionophore (**6**) selectively complexes, electrochemically recognises, and responds to the potassium guest cation in the presence of equimolar amounts of sodium and magnesium ions.

With a view to advancing chemical sensor technology, modelling electron transfer processes in biological systems, and producing new redox catalysts, considerable interest is being shown in the syntheses of redox-active macrocylic receptor molecules that contain a redox centre in close proximity to a host binding site.[1,2] These systems can be designed to electrochemically recognise the binding of, in principle depending on the complementary nature of the host cavity, a cationic,[3—7] anionic,[8] or neutral[9] inorganic or organic guest specie either through space interactions or *via* various bond linkages between the receptor site and redox centre. Obviously *selective* binding of a particular guest specie coupled with an electrochemical response is of paramount importance for potential prototypes of new amperometric molecular sensory devices. This communication demonstrates for the first time the concept of *selective* electrochemical recognition by reporting the synthesis of a new ferrocenyl ionophore (**6**) that selectively electrochemically detects the potassium guest cation in the presence of equimolar amounts of sodium and magnesium ions.

Table 1. Electrochemical data.

Compound	(**6**)/mV
$E_{1/2}$[a]	+340
$\Delta E\,(Na^+)$[b]	55
$\Delta E\,(K^+)$[b]	35
$\Delta E\,(Mg^{2+})$[b]	110
$\Delta E\,(Na^+/K^+)$[c]	35
$\Delta E\,(Na^+/K^+/Mg^{2+})$[c]	40

[a] Obtained in acetonitrile solution containing 0.2 M $[Bu^n_4N]BF_4$ as supporting electrolyte. Solutions were *ca.* 3×10^{-3} M in compound and potentials were determined with reference to a standard calomel electrode at 21 ± 1 °C at 0.2 V s^{-1} scan rate. [b] One wave anodic shifts in oxidation potential produced by presence of metal cation (4 equiv.) added as their perchlorate salts. [c] One wave anodic shift in oxidation potential produced by the presence of an equimolar mixture of cations (4 equiv.).

The reaction of 1,1′-bis(hydroxymethyl)ferrocene (**1**)[10] with phosphorus tribromide gave the unstable dibromide ferrocene derivative (**2**)[11] which on addition of an excess amount of triphenyl phosphine precipitated the new bis phosphonium salt (**3**). Treatment of (**3**) with two equivalents of n-butyl-lithium afforded the bis ylide (**4**) which on reaction with two moles of 4-formylbenzo-15-crown-5 (**5**)[12] gave the new ferrocenyl ionophore (**6**) as an orange–red solid (m.p. 153—154 °C) in 55% overall yield from (**3**) (Scheme 1). Satisfactory elemental analyses, FAB MS, and ^1H and ^{13}C NMR spectroscopy characterised the host's structure.†

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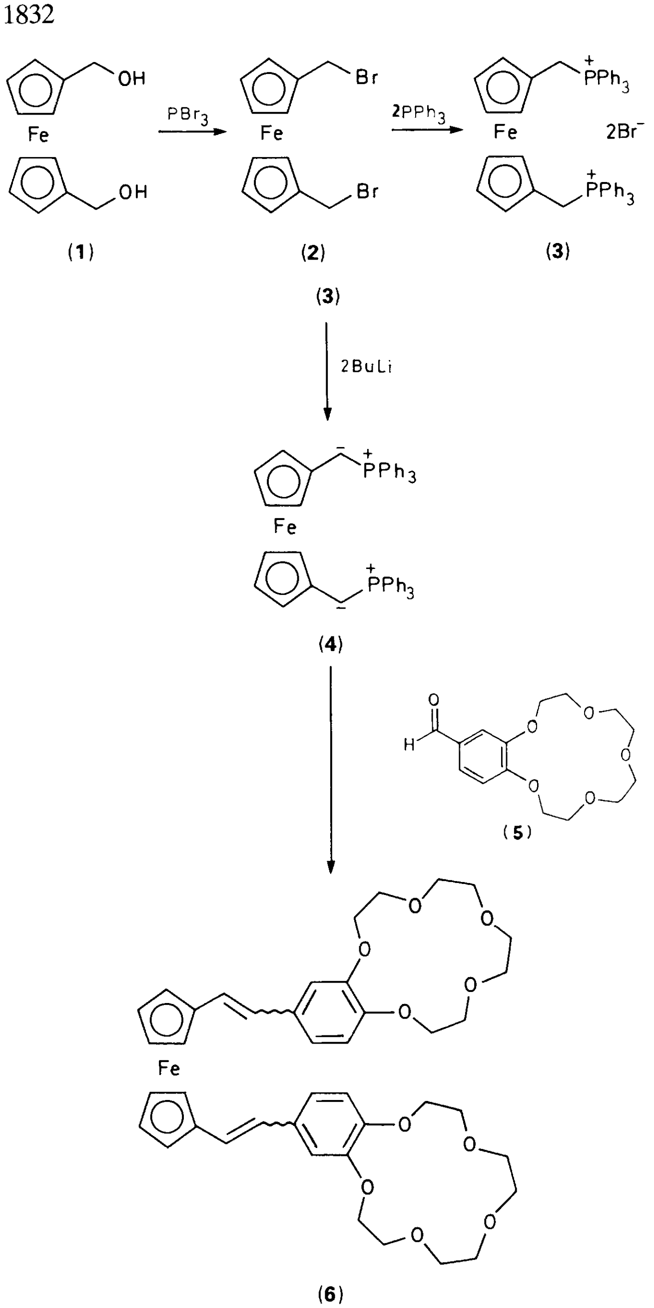
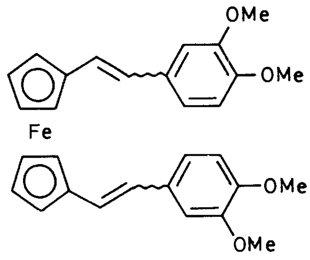
† Compound (**6**) is a mixture of three isomeric components, the *cis–cis, cis–trans*, and *trans–trans* isomers which have not yet been successfully separated. The same mixture of isomers was used throughout the subsequent FAB MS and electrochemical experiments.



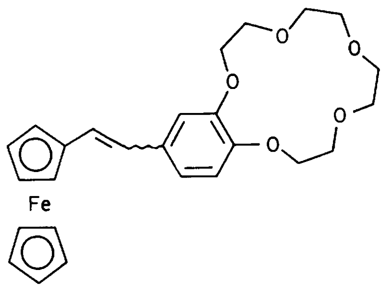
Scheme 1

Refluxing aqueous methanolic solutions of (**6**) with excess amounts of sodium and potassium hexafluorophosphates yielded orange crystalline solids of respective stoicheiometry $[(\mathbf{6})\cdot 2Na](PF_6)_2$ and $[(\mathbf{6})\cdot K]PF_6$ suggesting that one Na^+ is bound in each of the two benzo-15-crown-5 ether moieties of (**6**) whereas the larger K^+ forms a 1:1 intramolecular sandwich complex.

FAB MS has been used to study the selectivity of monocyclic crown ethers for Group IA metal cations in competition experiments[13] and we have recently successfully applied this technique to bis crown ether ligands.[14,15] The FAB MS competition experiment of (**6**) [5×10^{-3} M, methanol (1.0 ml)] with the nitrates of sodium,‡ potassium, rubidium, and caesium [5×10^{-3} M, water (0.5 ml)–glycerol (1.0 ml)] gave gas phase complex ions of $[(\mathbf{6}) + K]^+$ ion (*m/z* 809) and a minor peak $[(\mathbf{6}) + Rb]^+$ ion (*m/z* 855) exclusively. The relative peak intensities suggest a selectivity order of $K^+ > > Rb^+ > > > Na^+$, Cs^+ indicative of the 'bis crown effect'[16] exhibited by related bis-benzo-15-crown-5 crown ether ligands.



(**7**)



(**8**)

The electrochemistry of (**6**) was investigated in acetonitrile solution by cyclic voltammetry with $[Bu^n{}_4N]BF_4$ as the supporting electrolyte. The cyclic voltammograms were also recorded after addition of calculated equivalents of Na^+, K^+, and Mg^{2+}, equimolar mixtures of Na^+/K^+ and $Na^+/K^+/Mg^{2+}$ and the results obtained are presented in Table 1.

All the metal cations induced one wave anodic shifts in the redox potential of the ferrocenyl redox couple with Mg^{2+} having the largest charge to radius ratio producing the greatest magnitude of anodic shift. Negligible shifts ($\Delta E \leqslant 5$ mV) were observed with the model compound (**7**) and it is noteworthy that the magnitudes of these anodic shifts of the redox couple of (**6**) resulting from Na^+, K^+, and Mg^{2+} addition are approximately double those induced by the same metal cations on the redox couple of the mono substituted alkenic ionophore (**8**).[17]§

Of particular relevance to chemical sensor technology are the novel results of the electrochemical competition experiments. When an equimolar mixture of Na^+/K^+ or $Na^+/K^+/Mg^{2+}$ cations is added to electrochemical solutions of (**6**), the ferrocene/ferricinium redox couple shifts anodically by an amount approximately the same as that induced by the K^+ cation alone. This observation, together with the FAB MS competition experimental findings, suggests that the new ferrocenyl ionophore (**6**) is a first generation prototype potassium selective amperometric sensor, capable of detecting the K^+ cation in the presence of Na^+ and Mg^{2+} ions.

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‡ The non-competitive FAB MS experiment of (**6**) + $NaNO_3$ gave an ion for $[(\mathbf{6}) + Na]^+$ only.

§ Although (**6**) exists as a mixture of three isomeric components their individual electrochemical co-ordination chemical behaviour is expected to be the same because of the precedence of insignificant differences found between the magnitudes of the metal cation induced anodic shifts in the ferrocenyl redox potentials of the respective separated *cis* and *trans* isomers of (**8**).[17]

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