A New Bipyridinium Bis Benzo Crown Ether Ligand whose Redox Properties are Dependent upon Complexed Cation Induced Conformational Switching Effects

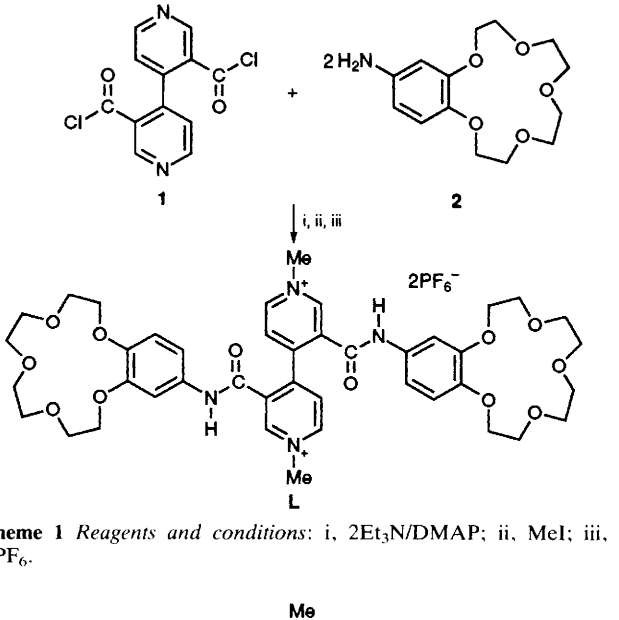
Paul D. Beer,* Zheng Chen, Alan Grieve and Jane Haggitt

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR

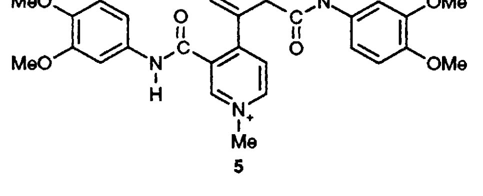
The synthesis, coordination and electrochemical properties of a novel 4,4'-bipyridinium bis benzo-15-crown-5 ligand are described whose group 1, 2 metal and ammonium cation redox-responsive behaviour is dependent upon cation induced conformational switching effects.

Cation and anion guest electrochemical recognition by redox-active ionophores is currently an area of intense activity of relevance to the development of amperometric sensing devices.[1] These systems typically have a reducible or oxidisable redox centre covalently linked to a nearby host binding site such as a crown ether. The nature of this bond linkage can have a profound effect on the electrochemical recognition process. In the case of ferrocenyl bis benzo crown ethers efficient through bond redox centre-crown ether complexed metal cation electrostatic communication occurs when the linkage is a highly delocalised conjugated π system such as vinyl[2] whereas amide (CONH)[3] and saturated alkyl linkages[4] exhibit insulating effects. We report here a new approach to charged guest electrochemical recognition through the design of a novel 4,4'-bipyridinium amide linked bis benzo crown ether ligand **L** whose redox responsive behaviour towards group 1, 2 and ammonium cationic guest species is dependent upon conformational switching effects induced by cation crown ether binding.[5]

The condensation of 3,3'-bischlorocarbonyl-4,4'-bipyridine **1**[6] with 2 equiv. of 4-aminobenzo-15-crown-5 **2**[7] gave the corresponding bis crown ether compound which on reaction with excess methyl iodide in acetonitrile solution produced an orange precipitate. Dissolution in water and addition of a saturated aqueous solution of $LiPF_6$ precipitated **L** as an orange solid in 51% overall yield (Scheme 1). An analogous synthetic procedure using 4-amino veratrole gave the model bipyridinium compound **5** in 55% overall yield.†



Scheme 1 *Reagents and conditions*: i, $2Et_3N$/DMAP; ii, MeI; iii, $LiPF_6$.



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Solution ^1H NMR and UV–VIS electronic spectroscopic cation titration experiments in acetonitrile with **L** suggested Ba^{2+}, K^+ and NH_4^+ guest cations formed 1 : 1 intramolecular sandwich complexes whereas 2 : 1 metal : ligand stoichiometric complexes were observed for the smaller Mg^{2+} and Na^+ cations. Stability constants were calculated from the electronic spectral titration data for the 1 : 1 complexes using SPECFIT and the log *K* values suggest **L** exhibits the selectivity sequence Ba^{2+} (log $K = 5.5$) > K^+ (log $K = 4.4$) > NH_4^+ (log $K = 3.9$). Solid-state Ba^{2+} and K^+ complexes of **L** were isolated whose elemental analyses were in accordance with 1 : 1 stoichiometry. In the case of the barium complex crystals suitable for an X-ray crystallographic determination were grown from a dilute aqueous solution of **L** : $Ba(ClO_4)_2$.‡ Two views of the crystal structure are shown in Fig. 1. The barium cation is ten coordinate bound between the two crown ether moieties adopting the solution predicted intramolecular sandwich complex conformation. Fig. 1(*b*) illustrates the dihedral angle between the two pyridinium groups, C_{12}–C_{11}–C_{41}–C_{42} is 60.3°.

The redox and electrochemical cation recognition properties of **L** and **5** were investigated in acetonitrile using cyclic voltammetry and the results for **L** are summarised in Table 1. Both compounds display two reversible one-electron reduction waves which in the case of **5** were not perturbed ($\Delta E \leqslant 5$ mV) in the presence of excess amounts of group 1, 2 metal or ammonium cations. In contrast ligand **L** exhibits novel electrochemical cation recognition behaviour. With Ba^{2+}

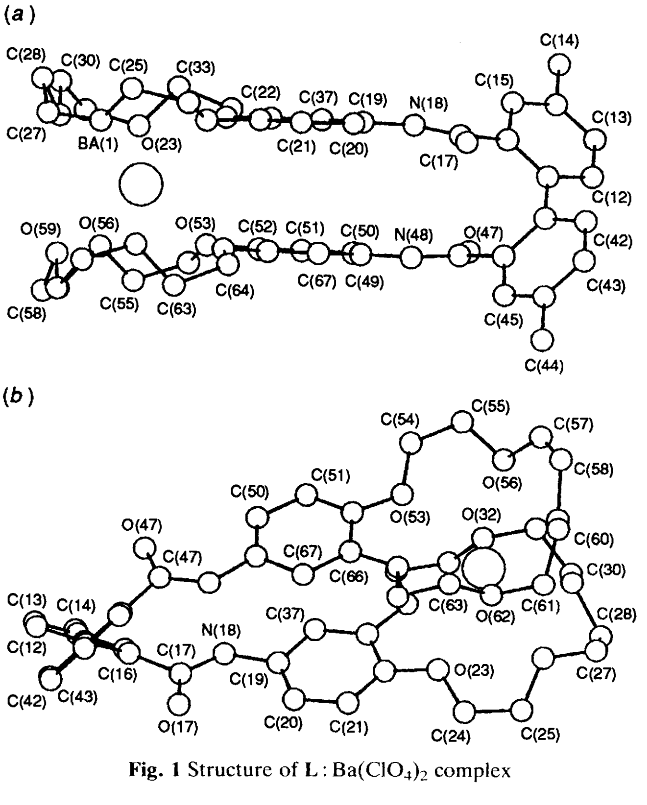

Fig. 1 Structure of **L** : $Ba(ClO_4)_2$ complex

Table 1 Electrochemical data for **L**

	Redox Couple	
	2+/1+	1+/0
$E_{\frac{1}{2}}/V^{a}$	−0.73	−0.87
$\Delta Ep/mV^{b}$	70	70
$\Delta E(Ba^{2+})/mV^{c}$	45	−10
$\Delta E(K^{+})/mV^{c}$	10	−40
$\Delta E(NH_4^{+})/mV^{c}$	10	−40
$\Delta E(Na^{+})/mV^{c}$	−10	30

[a] Obtained in acetonitrile containing 0.2 mol dm^{-3} ($Bu^n_4NBF_4$) as supporting electrolyte. Solutions were *ca.* 2 × 10^{-3} mol dm^{-3} in ligand and potentials were determined with reference to a Ag/Ag$^+$. [b] Separation between anodic and cathodic peak potentials of cyclic voltammograms; values for ferrocene under the same conditions ranged from 70–90 mV. [c] One-wave shift in oxidation potential produced by the presence of cations (4 equiv.) added as $Ba(ClO_4)_2$ and hexafluorophosphate salts. Positive values indicate anodic shift, negative values indicate cathodic shift.

cations the 2+/1+ redox couple is significantly anodically shifted by 45 mV and a small cathodic shift (10 mV) of the 1+/0 redox couple also results. It is noteworthy that the monocations, K$^+$ and NH_4^+, cause similar redox responsive effects. With sodium cations completely different contrasting redox responsive behaviour is observed, a small *cathodic* shift of the 2+/1+ redox couple (10 mV) and an anodic perturbation of the 1+/0 couple (30 mV) results. These unique electrochemical cation recognition findings may be rationalised by considering cation induced conformational switching effects on the ligand **L**. The binding of Ba^{2+}, K$^+$ and NH_4^+ cations by **L** results in the formation of a 1 : 1 intramolecular bis benzo crown ether sandwich conformation which necessitates a significant twisting of the 4,4′-bipyridinium redox moiety (Fig. 1), whereas the formation of the 2Na$^+$: **L** complex does not comparatively require such a dramatic geometric change of the 4,4′-bipyridinium unit.§ We have shown from electrochemical cation recognition studies of ferrocene bis benzo crown ether ligand systems[2–4] that the amide CO–NH bond linkage is a poor communicator of electrostatic charge. The insulating nature of the amide linkage is borne out by the cation induced modified bipyridinium redox properties of **L** being independent of the polarisability (charge : radius ratio) of the particular cationic bound guest species (compare Δ*E* values for Ba^{2+}, K$^+$ and NH_4^+, Table 1), but are reliant upon the redox-active ligand's conformation, resulting from the respective 1 : 1 or 2 : 1 cation : **L** complexes. This conformational switching effect is currently being exploited in other 4,4′-bipyridinium macrocyclic ligand systems.

We thank the AFRC for a studentship to A. G. and the SERC for use of Mass Spectrometry Service, University College, Swansea.

Received, 26th July 1994; Com. 4/04592K

Footnotes

† All new compounds were fully characterised by elemental analyses, ^1H and ^{13}C NMR and FABMS.

‡ *Crystal Data* for **L** : $Ba(ClO_4)_2$: $C_{42}H_{54}Ba_1Cl_4N_4O_{29}$, $M = 1358.0$, $a = 10.062(1)$, $b = 16.538(1)$, $c = 17.682(1)$ Å, $\alpha = 99.141(6)$, $\beta = 95.674(5)$, $\gamma = 103.976(5)°$, U = 2789.8 Å^3, $F(000) = 1380$, $D_c = 1.62$ g cm^{-3}, $Z = 2$, Mo-Kα radiation (λ = 0.7107 Å), μ(Mo-Kα) = 9.96 cm^{-1}, Space group $P\bar{1}$.

Data were measured on an Enraf-Nonius CAD4 diffractometer in the range $1 \leqslant \theta \leqslant 24°$. 9439 reflections were collected of which 6278 were unique with $I \geqslant 3\sigma(I)$. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction based on Azimuthal scan data was applied.

The non-hydrogen atoms were located by direct methods (SIR92) and difference Fourier syntheses. The structure was refined using full matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms with full occupancy in the cation. The structure suffers from disorder in the two crown ether rings. Two of the carbons in each ring [C(27), C(28) and C(57), C(58)] have two-fold disorder. All the disordered C atoms were assigned 50% occupancy and were refined with isotropic thermal parameters.

The hydrogen atoms were placed in calculated positions (C–H = 1 Å) with $U_{iso} = 1.25\ U_{eq}$ of adjacent atom and the positions were not refined. The hydrogens on the water molecule were neither found or placed in calculated positions.

At convergence $R = 0.073$ and $R_w = 0.086$ for 640 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Rotating disk voltammetric experiments support the proposed respective 1 : 1 and 2 : 1 cation : **L** solution state structures.

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