Potassium cation induced switch in anion selectivity exhibited by heteroditopic ruthenium(II) and rhenium(I) bipyridyl bis(benzo-15-crown-5) ion pair receptors

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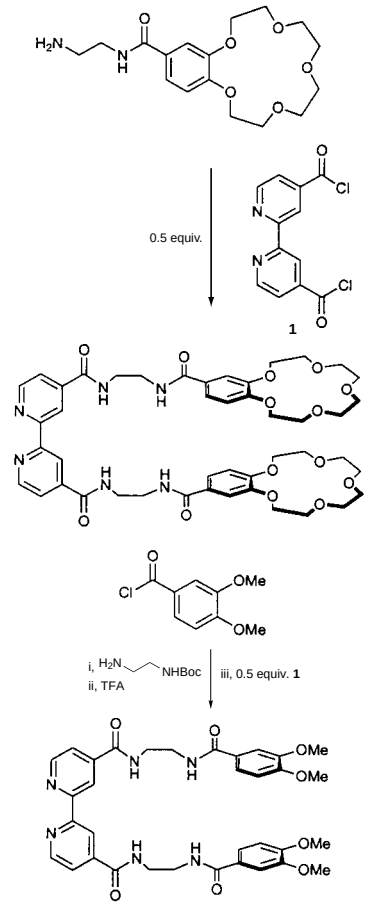
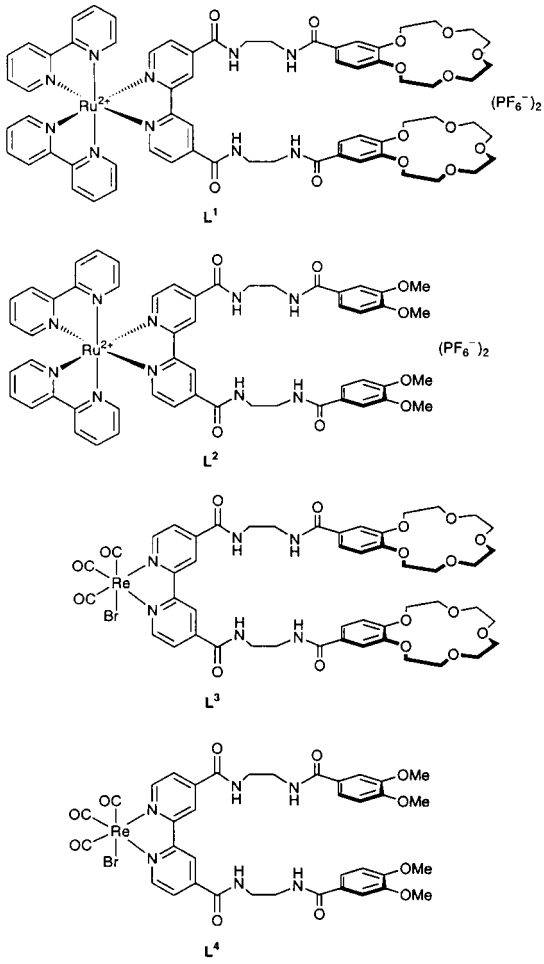
Cl^- and $H_2PO_4^-$ anion selectivity properties of new heteroditopic Ru^{II} and Re^{I} bipyridyl bis(benzo-15-crown-5) receptors are remarkably dependent upon the presence of co-bound intramolecular sandwich crown ether complexed K^+.

The design of new multisite ion pair receptors that contain covalently linked binding sites for both cations and anions is a new topical area of coordination chemistry.[1–6] In addition to being potential selective extraction/membrane transportation reagents for metal salts these ditopic ligand systems can be tailored to exhibit novel cooperative and allosteric behaviour whereby the complexation of one charged guest can influence, through electrostatic and conformational effects, the subsequent coordination of the pairing ion. We report here the synthesis of new heteroditopic Ru^{II} and Re^{I} bipyridyl bis(benzo-15-crown-5) receptors whose selectivity towards Cl^- and $H_2PO_4^-$ anionic guest species is remarkably dependent upon allosteric conformational and electrostatic effects of co-bound intramolecular sandwich crown ether complexed K^+ cations.

The synthetic routes to preparing the bipyridyl amide functionalised mono- and bis(benzo-15-crown-5) ligands and 3,4′-dimethoxyphenyl appended analogues are shown in Scheme 1. Reaction with $[RuCl_2(bipy)_2]$ followed by NH_4PF_6 and with $[Re(CO)_5Br]$, respectively, afforded the new receptors L^1–L^4 in good yields (Scheme 2). The K^+ cation and both Cl^- and $H_2PO_4^-$ anion coordination properties of the receptors were investigated by ^1H and in some instances by ^{13}C NMR titration experiments in $(CD_3)_2SO$ solution. The addition of KPF_6 to solutions of L^1 and L^3 caused the crown ether methylene carbons of the ^{13}C NMR spectra to significantly shift upfield by up to 0.6 ppm. Analysis of the resulting titration curves using the computer program EQNMR[7] suggested both receptors were forming 1 : 1 stoichiometric intramolecular sandwich bis crown ether complexes with K^+ with respective stability constant values of 350 and 540 M^{-1} for L^1 and L^3. The relatively smaller value of stability constant for L^1 may reflect the positively charged Ru^{II} centre electrostatically destabilising the crown ether bound K^+. Negligible shifts were observed with L^2 and L^4 suggesting K^+ complexation only takes place at the crown ether binding sites. Significant downfield perturbations of the respective receptor's amide and H^3-bipyridyl protons were observed on the addition of NBu_4Cl and $H_2PO_4^-$ salts to $(CD_3)_2SO$ solutions of L^1–L^4 indicating the amide-bipyridyl vicinity of the receptor is the site of anion binding. In all cases with Cl^- the titration curves suggested 1 : 1 complex stoichiometry which was also observed with $H_2PO_4^-$ and L^1, L^3. Precipitation problems unfortunately prevented complete $H_2PO_4^-$ titration curves from being obtained with receptors L^2 and L^4. Where possible titrations with both anions were repeated in the presence of 2 equiv. of KPF_6 and EQNMR determined stability constant values for all these titration experiments are presented in Tables 1 and 2. As found previously with related simple acyclic transition metal bipyridyl amide derivatives[8] a comparison of Tables 1 and 2 reveals L^1 and L^3 exhibit a pronounced selectivity preference for $H_2PO_4^-$ over Cl^-. It is noteworthy that Table 1 explicitly shows that the bis crown ether containing receptors L^1 and L^3 exhibit substantial increases in the magnitudes of stability constant for Cl^- binding on addition of KPF_6 by nearly sixfold for L^3. Interestingly no such increase in stability constant value is displayed by receptors L^2 and L^4 which do not contain crown ether binding sites. In contrast Table 2 displays a dramatic decrease in the stability constant values for $H_2PO_4^-$ binding for L^1 and L^3 on addition of KPF_6. The important consequence of which is the presence of K^+ can in principle induce a novel switch in the anion selectivity properties of both receptors. Tables 1 and 2 clearly illustrate the free receptors L^1, L^3 are $H_2PO_4^-$ selective whereas initial coordination of K^+ changes their anion selectivity preference to Cl^-. Repeating the titrations in the presence of tenfold excess of NBu_4PF_6 resulted in virtually no change in the determined stability constant values which negates simple ion pairing as a possible explanation for these positive and negative cooperative binding effects.



Scheme 1



Scheme 2

Table 1 Stability constants for Cl^- binding in the presence and absence of K^+ in $(CD_3)_2SO$

Receptor	K^a/M^{-1}
L^1	190
L^1 + 2 equiv. KPF_6	660
L^2	195
L^2 + 2 equiv. KPF_6	165
L^3	55
L^3 + 2 equiv. KPF_6	300
L^4	46
L^4 + 2 equiv. KPF_6	55

[a] Errors estimated to be ⩽10%.

The K^+ induced positive cooperativity of Cl^- binding may be a consequence of favourable electrostatic attraction between the crown ether bound K^+ and bipyridyl amide complexed anion, and, in addition be due to a favourable allosteric K^+ induced conformational effect. Solution formation of the 1 : 1 bis-benzo-15-crown-5 potassium cation intramolecular sandwich complex results in L^1 and L^3 forming a pseudo-macrocyclic preorganised structure which enhances Cl^- recognition but disfavours the binding of $H_2PO_4^-$ (Fig. 1). Of particular note is the structurally related macrocyclic receptor L^5 which exhibits remarkable thermodynamic stability and selectivity for Cl^- and does not bind $H_2PO_4^-$ phosphate at all in $(CD_3)_2SO$ solutions.[9]

Preliminary fluorescence emission spectroscopic measurements corroborate the NMR binding studies. The addition of Cl^- and $H_2PO_4^-$ to MeCN solutions of L^1 caused significant increases of up to 140% in luminescence intensity of the MLCT emission band (λ_{max} = 640 nm) with a concomitant hypsochromic shift of 7 nm. However in the presence of 1 equiv. of KPF_6 the subsequent addition of $H_2PO_4^-$ had very little effect on either the emission intensity or λ_{max}. In contrast with Cl^- a significant enhancement of intensity was observed.

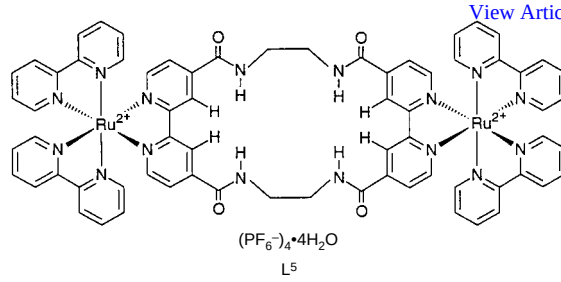


Table 2 Stability constants for $H_2PO_4^-$ binding in the presence and absence of K^+ in $(CD_3)_2SO$

Receptor[a]	K^b/M^{-1}
L^1	900
L^1 + 2 equiv. KPF_6	60
L^3	205
L^3 + 2 equiv. KPF_6	35

[a] Precipitation problems prevented complete titration curves from being obtained with L^2 and L^4 in presence and absence of KPF_6. [b] Errors estimated to be ⩽10%.

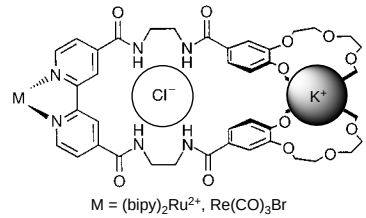


Fig. 1 Proposed solution structure of K^+Cl^- ion pair complex of L^1 and L^3. M = $Ru(bipy)_2^{2+}$ or $Re(CO)_3Br$

In summary the anion selectivity properties of new Ru^{II} and Re^{I} bipyridyl bis(benzo-15-crown-5) receptors can be dramatically switched *via* the binding of K^+ cations. In the absence of K^+ the receptors are selective for $H_2PO_4^-$ over Cl^-, whereas following the formation of the intramolecular K^+ bis crown sandwich complex the reverse selectivity Cl^- over $H_2PO_4^-$ is exhibited.

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Notes and References

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