Cooperative binding of potassium cation and chloride anion by novel rhenium(I) bipyridyl amide crown ether receptors

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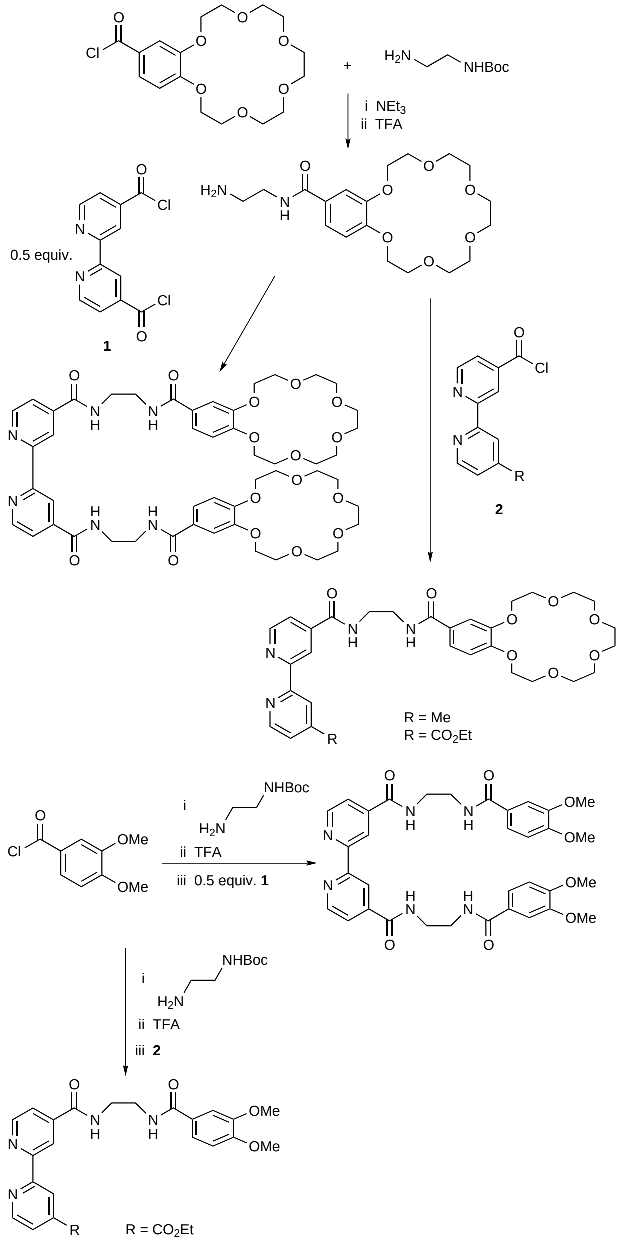
New rhenium(I) bipyridyl amide crown ether receptors are prepared and shown to complex K^+Cl^- ion pairs in which crown ether complexation of the potassium cation co-operates in the binding of chloride anion.

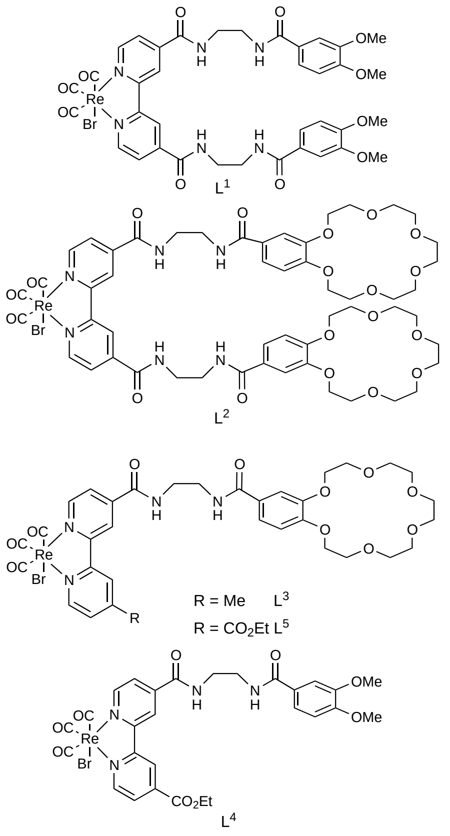
Ion pair recognition, the simultaneous binding of cationic and anionic guest species by ditopic receptors is a new emerging field of coordination chemistry.[1–5] These multisite ligand systems as well as being potential selective extraction/membrane transportation reagents for metal salts can also be designed to exhibit allosteric and cooperative behaviour whereby the binding of one charged guest can influence the subsequent coordination of the pairing ion. We have recently shown that charged or neutral transition metal organometallic and coordination amide containing receptors can selectively bind and sense anionic guest species.[6] The covalent attachment of benzo crown ether metal cation recognition sites to these anion receptors will create novel ion pair binding reagents. We report here the synthesis and preliminary coordination chemistry of new neutral rhenium(I) bipyridyl amide crown ether receptors that complex potassium cations and simultaneously bind chloride anions with positive cooperativity which is a first step towards the design of ion pair recognition systems.

The bipyridyl amide functionalised benzo-18-crown-6 and 3,4-dimethoxyphenyl ligands were prepared in good yields according to Scheme 1. Reaction of each of these bipyridyl ligands with $[Re(CO)_5Br]$ in THF produced the target receptors L^1–L^5 as yellow solids (Scheme 2). The potassium cation and chloride anion coordination properties of the receptors were investigated by ^1H NMR titration experiments in $(CD_3)_2SO$ solution. The addition of KPF_6 to ^1H NMR solutions of L^2, L^3 and L^5 caused the crown ether methylene protons to significantly shift to lower field. Analysis of the resulting titration curves with the computer program EQNMR[7] suggested the respective crown ether recognition site of each receptor to form a 1 : 1 complex with the potassium cation, with stability constant values of *ca*. 500 $dm^3\ mol^{-1}$ for L^3 and L^5. Negligible shifts were observed with L^1 and L^4 suggesting K^+ complexation only takes place at the crown ether binding sites. The addition of tetrabutylammonium chloride to $(CD_3)_2SO$ solutions of L^1–L^5 caused significant downfield perturbations of the respective receptor's amide and H^3-bipyridyl protons by up to $\Delta\delta = 0.55$ ppm, indicating anion binding is taking place exclusively in the amide-bipyridyl vicinity of the receptor. In all cases the titration curves suggested 1 : 1 complex stoichiometry. The titrations with chloride were repeated in the presence of 2 equiv. of KPF_6 and EQNMR[7] determined stability constant values for both titration experiments are presented in Table 1. Table 1 clearly shows the addition of KPF_6 to the crown ether containing receptors L^2, L^3 and L^5 leads to a substantial increase in the magnitude of stability constant, by nearly threefold for L^2, for the respective chloride anion receptor-complex. It is noteworthy that receptors L^1, L^4, lacking crown ether moieties, do not exhibit such an increase in stability constant in the presence of KPF_6 which suggests the origin of positive co-operativity is an intramolecular electrostatic attraction between a simultaneously crown ether bound potassium cation and bipyridyl amide complexed chloride anion.

Receptor L^3 was co-crystallized with KCl and the X-ray crystal structure of the ion-pair complex $[L^3KCl]_2\cdot 2H_2O$ which has a crystallographic centre of symmetry is shown in Fig. 1 and 2.†‡



Scheme 1



Scheme 2

Table 1 Stability constants for chloride anion binding in the presence and absence of potassium cations in $(CD_3)_2SO$

Receptor	K^a/dm^3 mol^{-1}
L^1	44
$L^1 + KPF_6$ (2 equiv.)	46
L^2	48
$L^2 + KPF_6$ (2 equiv.)	120
L^3	24
$L^3 + KPF_6$ (2 equiv.)	57
L^4	15
$L^4 + KPF_6$ (2 equiv.)	15
L^5	—^{b}
$L^5 + KPF_6$ (2 equiv.)	35

^{a} Errors estimated to be ⩽5%. ^{b} Very weak binding, a stability constant could not be determined.

In the Re(CO)$_3$(bipy) moieties, the environment of the metal is octahedral with dimensions in the expected range. Each bipy is linked *via* an amide group to a benzo-18-crown-6 in which is encapsulated a potassium ion. The benzo crown has a planar conformation with the six oxygens coplanar to within 0.10 Å with the potassium 0.24 Å from the plane. The hexagonal bipyramidal potassium coordination is completed by two axial bonds to a water molecule and to an amide oxygen atom from another substituted Re(CO)$_3$(bipy) moiety, thus forming the centrosymmetric dimer. The chloride anion is disordered over two positions 1.07 Å apart with relative occupancies 56 and 44%, but each anion is hydrogen bonded to both amide nitrogen atoms, Cl(21) to N(63) at 3.25 and N(66) at 3.41 Å and Cl(22) to N(63) 3.12 and N(66) at 3.29 Å.

In summary, these new rhenium(I) bipyridyl amide crown ether receptors are capable of binding K^+Cl^- ion pairs in which crown ether complexation of the potassium cation co-operates in the complexation of chloride anion.

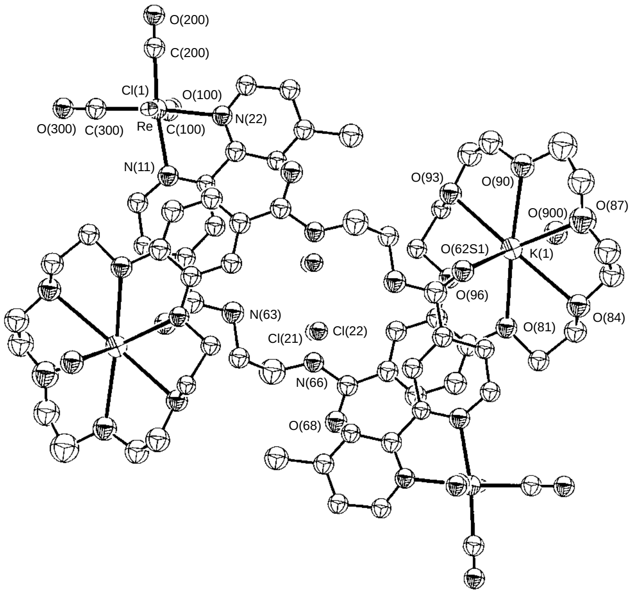


Fig. 1 The centrosymmetric dimer $[L^3KCl]_2{\cdot}2H_2O$ with ellipsoids shown at 20% probability together with the atomic numbering scheme. Bond lengths from the potassium to crown oxygens are to O(81) 2.752(13), O(84) 2.913(15), O(87) 2.76(2), O(90) 2.801(16), O(93) 2.881(13), O(96) 2.722(14) Å and to the amide oxygen O(62S1) 2.654(17) and to the water molecule O(900) 2.753(17) Å.

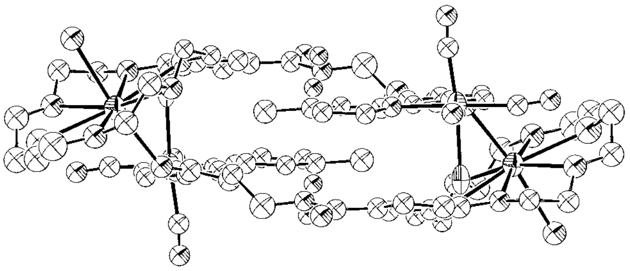


Fig. 2 The centrosymmetric dimer $[L^3KCl]_2{\cdot}2H_2O$ with ellipsoids shown at 20% probability

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Footnotes and References

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† *Crystal data*: $C_{68}H_{76}Cl_4K_2N_8O_{24}Re_2$, M = 1981.76, triclinic, space group $P1$, Z = 1, a = 11.445(12), b = 14.668(17), c = 16.328(17) Å, α = 115.27(1), β = 90.02(1), γ = 112.34(1)°, U = 2249 Å^3, D_c = 1.463 Mg m^{-3}, μ = 29.69 mm^{-1}, $F(000)$ = 988, 7037 independent reflections, 1191 with $I > 2\sigma(I)$ refined on F^2 to R of 0.0808 for data with $I > 2\sigma(I)$. CCDC 182/697.

‡ A substitution of Br for Cl has occurred at the Re^I centre. During the NMR titrations no evidence of this reaction was ever seen over the course of the experiment for *ca.* 2 h.

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