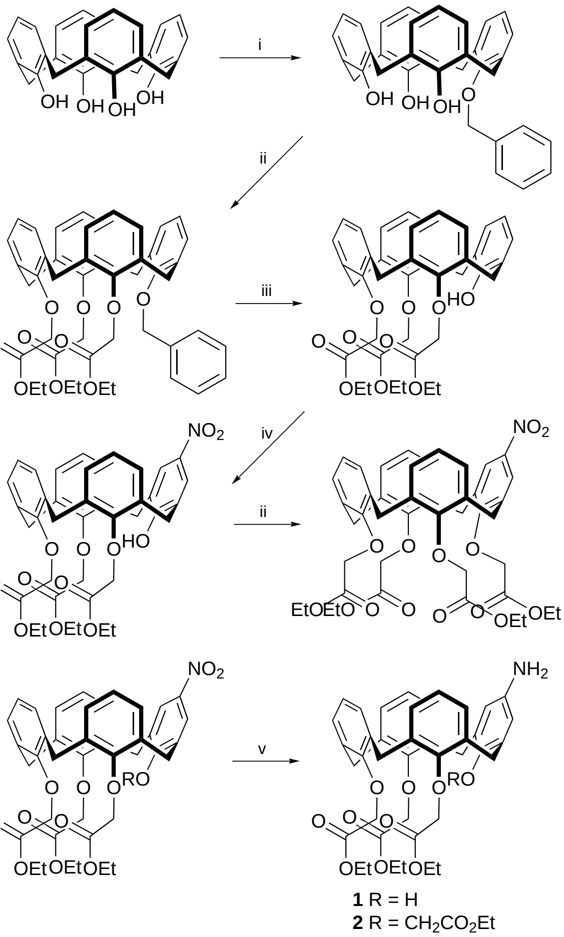
Alkali metal cation cooperative iodide anion recognition by new heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl receptor molecules

Paul D. Beer* and James B. Cooper

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

New heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl receptors are synthesised and shown to simultaneously bind alkali metal cations and iodide anion with positive cooperativity.

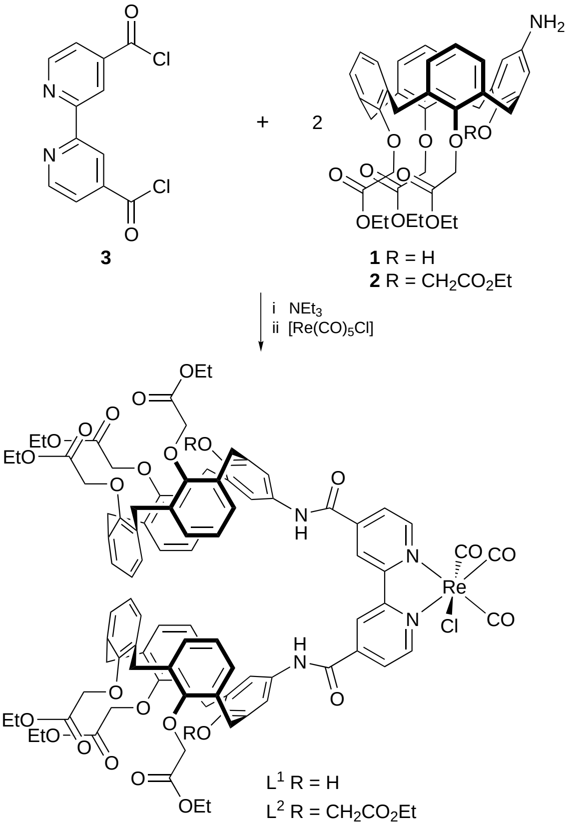
The design of new ditopic[1] ligands for the simultaneous complexation of anionic and cationic guest species is a new exciting area of coordination chemistry of significant relevance to the selective extraction and/or transportation of metal salts across lipophilic membranes. Rare examples of receptors containing appropriate covalently linked binding sites for anions and cations include Lewis-acidic boron,[2] uranyl,[3] polyammonium[4] centres combined with crown ether moieties and crown ether or urea functionalised calix[4]arene ionophores[5,6] which are capable of solubilising alkali metal salts into organic solvent media. We have shown that charged or neutral transition metal organometallic and coordination amide containing receptor systems can selectively bind and sense anions.[7] Lower rim ester functionalised calix[4]arenes are known to coordinate alkali metal cations.[8] Incorporating these two types of recognition sites on to the calix[4]arene building block will create potential heteroditopic receptors capable of binding anions and cations. We report here the syntheses of new heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl receptors which display positive cooperative upper rim binding of the iodide anion *via* lower rim complexation of alkali metal cations.



Scheme 1 *Reagents and conditions* i, 1 equiv. $PhCH_2Br$, 0.5 equiv. K_2CO_3, MeCN reflux, 24 h; ii, $BrCH_2CO_2Et$ (excess), K_2CO_3 (excess), MeCN reflux 48 h; iii, Pd/C, HCO_2NH_4, EtOH reflux; iv, NH_4NO_3, HCl, H_2O, acetic anhydride, CH_2Cl_2; v, Zn (excess), HCl (excess), reflux EtOH, 24 h

The new upper rim mono-amine–lower rim ester substituted calix[4]arene derivatives **1** and **2** were prepared according to Scheme 1. Condensation reactions of 2 equiv. of **1** and **2** with 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine **3**[9] followed by complexation with $Re(CO)_5Cl$ gave the new receptors L^1 and L^2 in good yields (Scheme 2).

The cation and anion coordination properties of both receptors were investigated by ^1H NMR titration experiments in CD_3CN solution. The addition of $LiClO_4$, $NaClO_4$ and KPF_6 salts typically caused the ester methylene receptors' protons to initially broaden and sharpen again after 2 equiv. suggesting complexes of $2M^+:L$ stoichiometry are being formed in



Scheme 2

Table 1 Stability constants for iodide binding in the presence and absence of alkali metal cations in CD_3CN

Receptor	Metal cation[b]	K^a/dm^3 mol^{-1}
L^1	None	67
L^1	Li^+	294
L^1	Na^+	202
L^1	K^+	100
L^2	None	40
L^2	Li^+	305
L^2	Na^+	322
L^2	K^+	209

[a] Errors estimated to be $\leqslant$5%. [b] Titration carried out in the presence of 2 equiv. of alkali metal cation salt, perchlorates for lithium, sodium and hexafluorophosphate for potassium.

solution, with the alkali metal cations coordinated at the lower rim ester recognition sites. The addition of tetrabutylammonium chloride, iodide and benzoate salts caused substantial downfield perturbations of the respective receptor's amide, H_3bipyridyl and aryl calix[4]arene protons indicating anion binding is taking place at the upper-rim bis(calix[4]arene) vicinity of the receptor. In all cases the resulting titration curves indicated 1 : 1 complex stoichiometry. Stability constants were calculated from the titration data using EQNMR[10] for complexation with iodide (Table 1). Unfortunately the anion complexes with Cl^- and $PhCO_2^-$ are so strong in CD_3CN that only a semi-quantitative estimate of the value of $K > 10^4$ dm^3 mol^{-1} could be made. The ^{1}H NMR iodide titration experiments were repeated in the presence of 2 equiv. of alkali metal salt and the stability constant values are presented in Table 1. Clearly with both receptors there is a significant increase in the strength of iodide binding when the alkali metal cations are co-bound by nearly an order of magnitude in the case of L^2 and sodium cations. This positive cooperative binding of the iodide anion may be attributed to each lower rim ester complexed metal cation rigidifying the calix[4]arene structure in such a way as to preorganise the upper rim for anion binding.[11] Also through bond electrostatic effects of the complexed metal cation may enhance the relative acidity of the receptors' amide protons and lead to stronger hydrogen bonding with the iodide guest anion. Interestingly Table 1 shows that receptor L^2 exhibits the largest positive cooperative iodide anion binding effect with the sodium cation, which is known to form highly selective complexes with lower rim tetrasubstituted ethyl ester calix[4]arenes.[8]

In conclusion these new heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl receptors are capable of simultaneously binding alkali metal cations and iodide anion with positive cooperativity.

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Footnote and References

* E-mail: paul.beer@icl.ox.ac.uk

1 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89.

2 M. T. Reetz, C. M. Niemeyer and K. Harris, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1472.

3 D. M. Rudkevich, Z. Brzozka, M. Palys, H. C. Visser, W. Verboom and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 467.

4 K. I. Kinnear, D. P. Mousley, E. Arafar and J. C. Lockhart, *J. Chem. Soc., Dalton Trans.*, 1994, 3637.

5 P. D. Beer, M. G. B. Drew, R. J. Knubley and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1995, 3117.

6 J. Scheerder, J. P. M. van Duynhoven, J. F. J. Engbersen and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1090.

7 P. D. Beer, *Chem. Commun.*, 1996, 689 and references therein.

8 F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marques, B. L. Ruhl, M. J. Schwing-Weill and E. M. Seward, *J. Am. Chem. Soc.*, 1989, **111**, 8681.

9 C. P. Whittle, *J. Heterocycl. Chem.*, 1977, **14**, 191.

10 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311.

11 In ref. 6, lower rim complexation of alkali metal cations is essential for upper rim halide anion complexation.

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