Solvent dependent anion selectivity exhibited by neutral ferrocenoyl receptors

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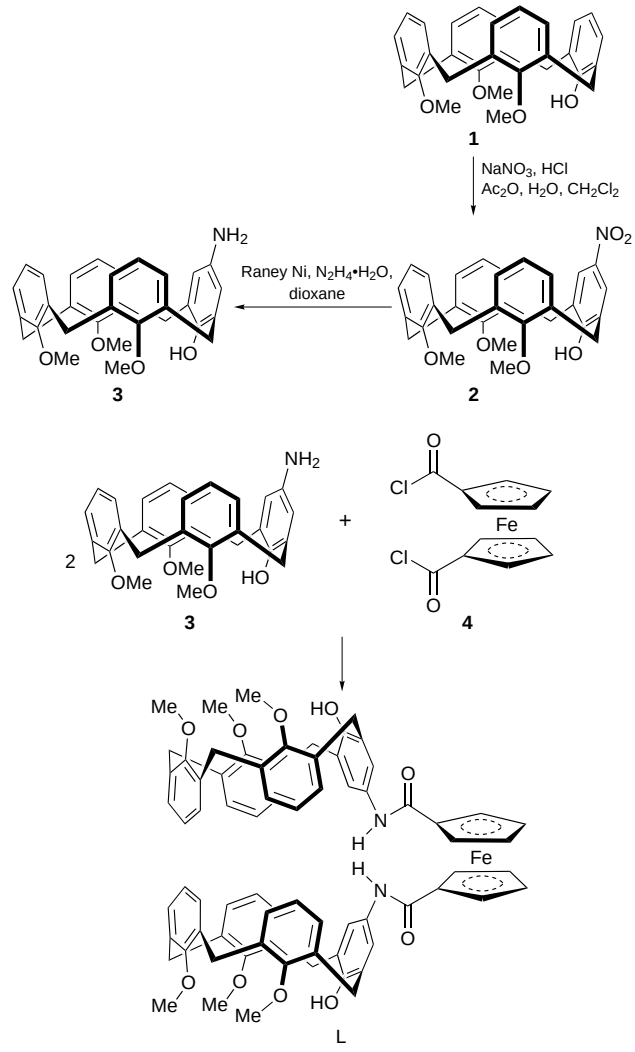
The nature of the solvent medium dramatically alters the anion recognition properties of a new bis(calix[4]arene) ferrocenoyl receptor L by influencing both the magnitude of stability constants and the anion binding selectivity trend the receptor displays.

The recognition of anionic guest species of biochemical, medical and environmental importance by positively charged or neutral abiotic receptor molecules is an area of ever increasing research activity.[1] Although a wide range of solvents and solvent mixtures have been used in anion binding studies relatively little attention has been paid as to how the nature of the solvent affects the stability of anion–receptor complexes[2] and perhaps more importantly the anion selectivities of the receptors. We report here a preliminary investigation into the complexation of a number of anions in a range of solvents by a new neutral, amide functionalised ferrocenoyl bis(calix[4]arene) receptor[3] and demonstrate the novel finding that the solvent medium alone can dramatically influence the anion selectivity preference of a particular neutral amide containing receptor.

The trimethoxy lower-rim substituted calix[4]arene compound **1**[4] was treated with sodium nitrate and hydrochloric acid to produce the nitro derivative **2** in 80% yield. Using Raney nickel and hydrazine hydrate, **2** was reduced to the amine **3** and immediately condensed with 1,1′-bis(chlorocarbonyl) ferrocene **4**[5] to afford the new ferrocenoyl-bis(calix[4]arene) L as an orange solid in 82% yield (Scheme 1).

The anion coordination properties of L were investigated by ^{1}H NMR anion titration experiments in CD_2Cl_2, CD_3CN and $(CD_3)_2CO$ solutions with tetrabutylammonium chloride, benzoate and acetate salts. Significant downfield perturbations of the receptor's amide, cyclopentadienyl and upper-rim calix aromatic protons *ortho* to the amide groups were observed in all solvents suggesting anion binding is taking place at the bis(calix[4]arene)–ferrocenoyl upper-rim vicinity of the receptor. Stability constants were calculated from the resulting titration curves using EQNMR[6] and these values are presented in Table 1, and, for comparison purposes, Table 2 displays stability constant data for the non-calix[4]arene receptor **5**. It is immediately apparent from both Tables that the solvent exerts a very great effect on the complex equilibrium between the receptor and anionic guest with the magnitude of stability constant varying by over two orders of magnitude in some cases. A comparison of the data shows that there is no obvious relationship between complex stability and bulk solvent properties such as relative permittivity (ε) and dipole moment (μ). It is noteworthy however, that there is a correlation between the stability constant values and the Gutmann acceptor number (AN) of the solvent,[7] which gives a quantitative measure of the solvent's hydrogen-bond donor ability. Both Tables show that as AN decreases, the stability constant values increase. A solvent with a greater AN acts as a more effective hydrogen-bond donor so solvates anions to a greater extent and competes with the receptor for binding of the anion. What is of real significance is the observation that the anion selectivity preferences of both receptors change as the solvent AN decreases. L exhibits the solvent dependent selectivity trends (CD_2Cl_2) $PhCO_2^-$ > Cl^- > $MeCO_2^-$; (CD_3CN) $PhCO_2^-$ > $MeCO_2^-$ > Cl^-; [$(CD_3)_2CO$] $MeCO_2^-$ > Cl^- > $PhCO_2^-$ while **5** shows (CD_2Cl_2) $PhCO_2^-$ ≈ $MeCO_2^-$ > Cl^-;

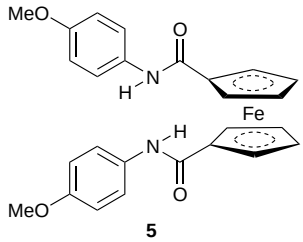


Scheme 1

Table 1 Solvent effects on the stability constant values of the anion complexes of L

				K^a/dm^3 mol^{-1}		
				Anion		
Solvent	ε	μ	AN	Cl^-	$PhCO_2^-$	$MeCO_2^-$
CD_2Cl_2	8.9	1.5	20.4	40	117	26
CD_3CN	36.0	3.96	18.9	70	360	120
$(CD_3)_2CO$	20.7	2.86	12.5	5200	940	6000

[a] Estimated errors < 10%; ε = relative permittivity, μ = dipole moment, AN = acceptor number of solvent.



5

Table 2 Solvent effects on the stability constant values of the anion complexes of **5**[a]

				K^b/dm^3 mol^{-1}		
				Anion		
Solvent	ε	μ	AN	Cl^-	$PhCO_2^-$	$MeCO_2^-$
CD_2Cl_2	8.9	1.5	20.4	175	215	210
$(CD_3)_2CO$	20.7	2.86	12.5	400	1500	3000

[a] Receptor **5** is insoluble in CD_3CN. [b] Estimated errors < 10%.

$[(CD_3)_2CO]$ $MeCO_2^-$ > $PhCO_2^-$ > Cl^-. These selectivity sequences may be rationalised in terms of relative anion solvation. As the hydrogen-bond donor ability of the solvent (AN) decreases the smaller, harder anions, acetate and chloride, become bound preferentially over the larger, charge diffuse benzoate. In the same manner that chloride and acetate are more heavily solvated in even very weakly protic solvents, in aprotic solvents they bind more strongly to the only protic source present, the ferrocene diamide receptor. As Tables 1 and 2 illustrate it can be concluded that the more heavily solvated anions are affected by changes in solvent to a greater extent than those which are less heavily solvated.

Interestingly with respect to receptor structure the introduction of the bis(calix[4]arene) cavity serves to amplify the solvent dependent anion stability constant values and selectivity effects. It can be seen from Tables 1 and 2 that the increases in stability constants (as AN decreases) for the bis(calix[4]arene) receptor are significantly larger than those for the non-calix[4]arene analogue **5**.

In conclusion the preliminary results presented here show that the nature of the solvent used in the study of anion binding by neutral hydrogen-bond donor receptors can determine both the magnitudes of stability constants and the anion binding selectivity. The selectivity of the receptors is best described in terms of the competition between the solvent and the receptor for the binding and solvation of the anions. The effect of the receptor's structure can be more clearly discerned when comparisons between stability constants and selectivities in different solvents are made and a suitable model compound is used.

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Footnotes and References

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