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Cooperative halide, perrhenate anion–sodium cation binding and pertechnetate extraction and transport by a novel tripodal tris(amido benzo-15-crown-5) ligand

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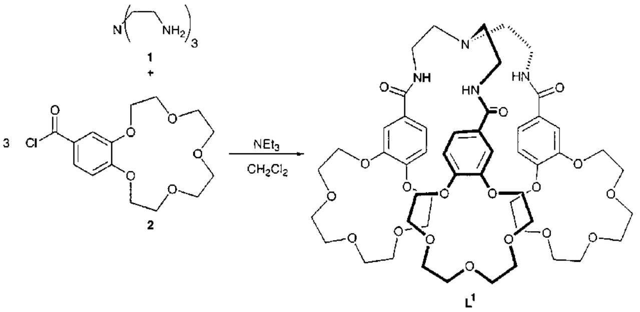
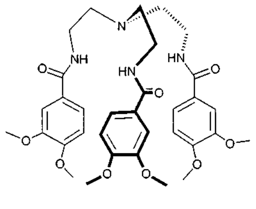
A new tripodal tris(amido benzo-15-crown-5) ligand L^1 cooperatively binds chloride, iodide and perrhenate anions *via* co-bound crown ether complexed sodium cations and efficiently extracts and transports the pertechnetate anion from simulated aqueous nuclear waste solutions *via* cooperative ion-pair binding effects.

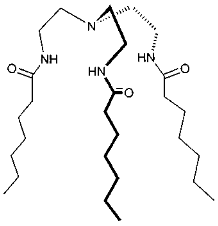
Ion pair recognition, the simultaneous complexation of cationic and anionic guest species by multisite receptors, is a new, emerging and topical field of coordination chemistry.[1–6] These heteroditopic ligands can be designed to exhibit novel cooperative and allosteric behaviour whereby the binding of one charged guest can influence, through electrostatic and conformational effects, the subsequent coordination of the pairing ion. Such systems have potential as new selective extraction and transportation reagents for ion pair species of environmental importance. As a consequence of discharges from nuclear fuel reprocessing plants the radioactive pertechnetate anion TcO_4^- is alleged to have a detrimental effect on the environment.[7] Approaches to the removal of pertechnetate anion from waste include liquid–liquid coextraction with metal complexed crown ethers,[8] lipophilic arsonium[9] and ferrocenium[10] salts and π-transition metal–cyclotriveratrylene derivatives.[11] In order to demonstrate, to the best of our knowledge for the first time, the practical usage of ion-pair cooperativity for extraction of such a toxic anionic guest species, we report here the synthesis of a new tripodal tris(amido benzo-15-crown-5) ligand L^1 that cooperatively binds halide and perrhenate anions *via* crown ether complexation of sodium cations, and also efficiently extracts and transports the pertechnetate anion from simulated aqueous nuclear waste *via* cooperative ion-pair binding effects. The target ligand L^1 containing a tripodal tetrahedral amide hydrogen bond donor anion recognition site in combination with crown ether cation binding moieties was synthesised in 55% yield by condensation of tris(2-aminoethyl)amine (tren) **1** with 3 equiv. of 4-chlorocarbonylbenzo-15-crown-5[12] **2** in the presence of Et_3N in CH_2Cl_2 (Scheme 1). Analogous synthetic procedures using appropriate acid chlorides were used to prepare the tripodal model ligands L^2 and L^3 in 30 and 29% yield respectively.



Scheme 1



L^2



L^3

The anion binding properties of L^1–L^3 were initially investigated by ^1H NMR titration studies with Cl^-, I^- and ReO_4^- in $CDCl_3$ solution. The latter two anions were chosen as I^- has approximately the same size and charge density as TcO_4^-, and ReO_4^- is an isostructural analogue. The addition of all three anions (as their Bu_4N^+ salts) to $CDCl_3$ solutions of L^1–L^3 caused significant downfield perturbations of the respective ligand's amide protons by up to $\Delta\delta$ = 1.41 ppm, indicating anion binding is taking place in the tripodal amide vicinity of the ligand. Analysis of the resulting titration curves with the computer program EQNMR[13] suggested 1 : 1 complex stoichiometry in all cases and the determined stability constant values are presented in Table 1. The magnitudes of the stability constants shown in Table 1 are relatively modest, reflecting the neutrality of the ligands; all three ligands exhibit the largest stability constant with chloride. Because nuclear waste discharges typically contain high concentrations of sodium cations it was of interest to investigate the mode of binding of this particular cationic guest to L^1. Unfortunately solubility problems prevented use of ^{13}C NMR titration techniques.† By monitoring the picrate chromophore, UV-visible spectroscopic titration experiments with sodium picrate and L^1 in 1 : 1 THF–CH_2Cl_2 indicated that at high concentrations of sodium cation (*i.e.* ⩾ 3 equiv.) unsurprisingly, one sodium cation is bound in each benzo-15-crown-5 moiety. However at lower concentrations, the observation of a well documented bathochromic shift of the picrate chromophore to 377 nm[14] indicated the additional presence of a 1 : 1 charge separated sandwich complex. Interestingly, alkali metal picrate extraction experiments with L^1 (Table 2) revealed an extraction preference for Na^+ > K^+ > Cs^+. In order to elucidate cooperative ion-pair binding effects

Table 1 Anion stability constant data

Ligand	K^a/M^{-1}		
	Cl^-	I^-	ReO_4^-
L^1	60	30	40
L^2	75	40	40
L^3	40	20	30

[a] Determined in $CDCl_3$ at 298 K, errors estimated to be ⩽10%. [L] = 1×10^{-2} M.

Table 2 Extraction of metal picrates by L[1]

Picrate	Extraction[a] (%)
Na	80
K	40
Cs	15

[a] Aqueous phase: 1×10^{-4} M metal picrate; $CDCl_3$ phase: 1×10^{-3} M L^1 at 298 K.

^1H NMR anion titration experiments with L^1 were repeated in the presence of 1 equiv. of sodium picrate and EQNMR determined stability constant values are present in Table 3. Clearly there is a significant increase in the strength of binding for all anions in the presence of 1 equiv. of sodium cation; in the case of ReO_4^- the increase is greater than twenty-fold. This positive cooperativity may be attributed to the increased electrostatic attraction between the positively charged $L^1{\cdot}Na^+$ complex and the guest anion. The complexed metal cation may also affect the spatial arrangement of the ligand and enhance the relative acidity of the ligand's amide protons, leading to stronger hydrogen bonding of the anionic guest. It is noteworthy that the anion selectivity trend displayed by L^1 is altered in the presence of sodium. With no metal cation present, L^1 binds Cl^- in preference to ReO_4^-, however on addition of sodium cation, ReO_4^- is more strongly bound (Table 3), which suggests the binding of the metal cation preorganises L^1 for tetrahedral anionic guest recognition.

Table 3 Stability constants for L^1 anion binding in the presence and absence of sodium picrate in $CDCl_3$

Anion	K/M^{-1}
Cl^-	60[a]
Cl^- $(+Na^+)$[b]	520[c]
I^-	30[a]
I^- $(+Na^+)$[b]	390[c]
ReO_4^-	40[a]
ReO_4^- $(+Na^+)$[b]	840[c]

[a] At 298 K, errors estimated to be ≤10%. [b] Titration carried out in the presence of 1 equiv. of sodium picrate. [c] At 298 K, errors estimated to be ≤15%.

Encouraged by these cooperative ion pair binding results, pertechnetate extraction experiments were carried out using conditions that simulated nuclear waste streams. The aqueous phase contained ammonium pertechnetate (100 ppm) and sodium nitrate (2.35 M) and the pH was adjusted to basic conditions (pH = 11) using NaOH. The organic phase consisted of CH_2Cl_2 solutions of L^1–L^3 and benzo-15-crown-5 at concentrations of 1.5×10^{-2} M for the tripodal ligands and 4.5×10^{-2} M for the crown ether. Equal volumes (2 ml) of each solution were mixed, and rapidly shaken. Inductively coupled plasma mass spectrometry (ICP-MS) and ^{99}Tc NMR were used to determine the concentrations of pertechnetate in the respective phases. L^1 extracted *ca.* 70% TcO_4^- whereas benzo-15-crown-5 achieved *ca.* 20% extraction after 5 min.‡ No increase in percentage extraction occurred after this time. Interestingly the tripodal ligands L^2 and L^3 containing no crown moieties displayed respectively less than 10 and 0% extraction of TcO_4^- even after 24 h. The distribution coefficients for TcO_4^- extraction by all the ligands are shown in Fig. 1. The distribution coefficient D for L^1 of 2.3 represents a greater than twenty-fold and ten-fold enhancement in extraction efficiency when compared to L^2 and benzo-15-crown-5, respectively. This important result suggests that a crown ether cation binding site covalently linked to a tripodal amide anion coordinating cavity creates a new efficient extraction reagent for TcO_4^- which operates *via* similar cooperative ion-pair binding effects as noted in the NMR titration experiments. Preliminary U-tube membrane transport investigations using the same aqueous conditions as described previously for the extraction experiments as the source of the aqueous phase revealed a six-fold increase in the rate of transport of TcO_4^- by L^1 (flux = 6.3×10^{-8} mol h^{-1}) over transport mediated by benzo-15-crown-5 (flux = 1.0×10^{-8} mol h^{-1}).

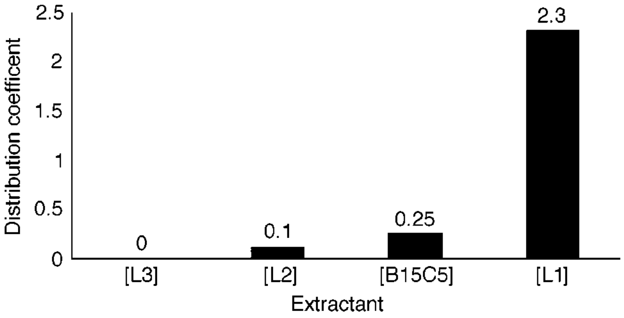


Fig. 1 Distribution coefficients for pertechnetate extraction by L^1–L^3 and benzo-15-crown-5. Organic phase: CH_2Cl_2, concentration of L^1–L^3 = 1.5×10^{-2} M, benzo-15-crown-5 = 4.5×10^{-2} M; aqueous phase: 100 ppm NH_4TcO_4, 2.35 M $NaNO_3$, pH 11, T = 298 K.

In summary, the new tripodal heteroditopic ligand L^1, by virtue of having both anion and cation recognition sites, has been demonstrated to cooperatively bind chloride, iodide and perrhentate anions *via* co-bound crown ether complexed sodium cations, and is a more efficient extraction and carrier transporting reagent for the pertechnetate anion when compared to monotopic ligands L^2, L^3 and benzo-15-crown-5.

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Notes and references

† ^1H NMR titration studies with L^1 and Na^+ unfortunately proved too complicated to monitor, to enable binding stoichiometries to be determined.

‡ In analogous extraction experiments at neutral pH, L^1 extracted 65% TcO_4^-.

1 M. T. Reetz, C. M. Niemeyer and K. Harris, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1472.
2 D. M. Rudkevich, Z. Brzozka, M. Palys, H. C. Visser, W. Verboom and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 467.
3 K. I. Kinnear, D. P. Mousley, E. Arafar and J. C. Lockhart, *J. Chem. Soc., Dalton Trans.*, 1994, 3637.
4 P. D. Beer, M. G. B. Drew, R. J. Knubley and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1995, 3117.
5 J. Scheerder, J. P. M. van Duynhoven, J. F. J. Engbersen and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1090.
6 J. E. Redman, P. D. Beer, S. W. Dent and M. G. B. Drew, *Chem. Commun.*, 1998, 231; P. D. Beer and S. W. Dent, *Chem. Commun.*, 1998, 825.
7 T. M. Beasley and H. V. Lorz, *Technetium in the Environment*, ed. G. Desmet and C. Myttenacrc, Elsevier, London, 1986.
8 M. G. Jalhoom, *J. Radioanal. Nucl. Chem.*, 1986, **104**, 131.
9 T. Omori, Y. Muraoka and H. Suganuma, *J. Radioanal. Nucl. Chem.*, 1994, **178**, 237.
10 J. F. Clark, D. L. Clark, G. D. Whitener, N. C. Schroeder and S. H. Strauss, *Environ. Sci. Technol.*, 1996, **30**, 3124.
11 J. L. Atwood, K. T. Holman and J. W. Steed, *Chem. Commun.*, 1996, 1401.
12 R. Ungaro, B. El Hay and J. Smid, *J. Am. Chem. Soc.*, 1976, **98**, 5198.
13 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311.
14 K. H. Wong, M. Bourgoin and J. Smid, *J. Chem. Soc., Chem. Commun.*, 1974, 715.

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