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Transition Metal Self-assembly of Dithiocarbamate Based Anion Receptors

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Novel macrocyclic and acyclic transition metal dithiocarbamate based anion receptors, prepared via metal mediated self-assembly, strongly bind anions, and in the case of L^2 electrochemically recognise carboxylate, chloride and dihydrogen phosphate.

Keywords: Anion recognition; Dithiocarbamate; Self-assembly

The synthesis of two- and three-dimensional macrocyclic and cage-like host molecules using metal directed self-assembly is a current area of intense research activity [1–8]. Through judicious choice of multidentate ligand and stereochemical requirement of the mediating metal ion the resulting self-assembled polymetallic structures may be designed to exhibit unique electronic/magnetic properties and have the potential to bind guest substrates [9–12]. Using for the first time the dithiocarbamate ligand [13] as a self-assembling construction motif we have recently synthesised novel nano-sized resorcarene-based zinc(II), cadmium(II) polymetallic assemblies which bind C_{60} [14,15] and copper(II)-dithiocarbamate macrocyclic molecular boxes capable of selectively sensing tetrahedral shaped anionic guest species ReO_4^- and $H_2PO_4^-$ using electrochemical techniques [16]. In an effort to construct new types of redox- and photo-active receptors for anion recognition using metal directed self-assembly we report here the synthesis of new acyclic and macrocyclic transition metal dithiocarbamate receptors (L^1–L^6) containing thiourea and amide hydrogen bond donor groups fashioned to bind and sense anions [17–19].

Condensation of ethylenediamine with two equivalents of chloroacetylchloride gave the bis-amide (**1**) which on reaction with hexylamine the bis-secondary amine (**2**) was isolated. Dithiocarbamate nickel(II), copper(II) and zinc(II) amide containing macrocyclic molecular boxes L^1–L^3 were prepared in a one-pot metal directed self-assembly synthesis by reaction of (**2**) with carbon disulphide, potassium hydroxide and metal acetate in yields of 60–70% (Scheme 1).

The reaction of mono-BOC protected ethylenediamine (**3**) with carbon disulfide followed

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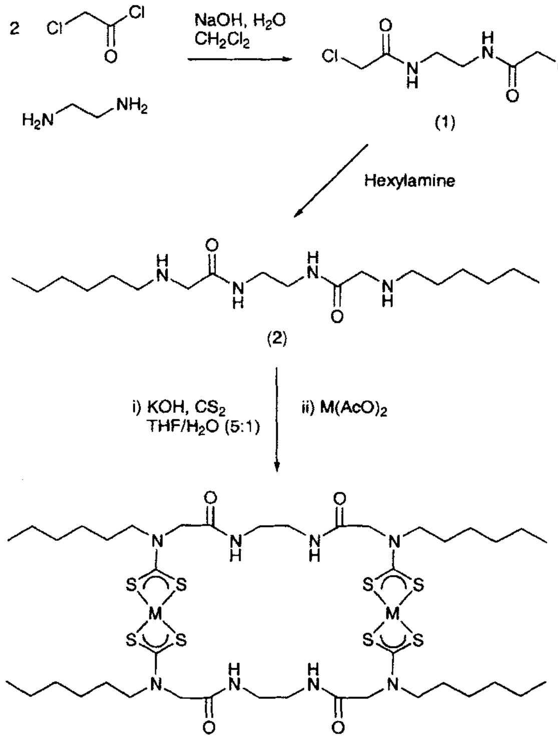


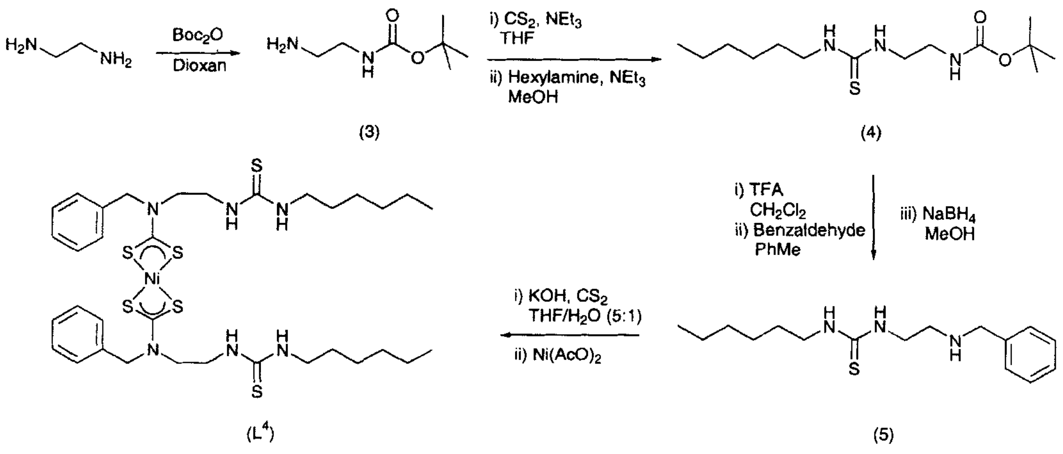
M = Ni (L^1), Cu (L^2), Zn (L^3)

SCHEME 1

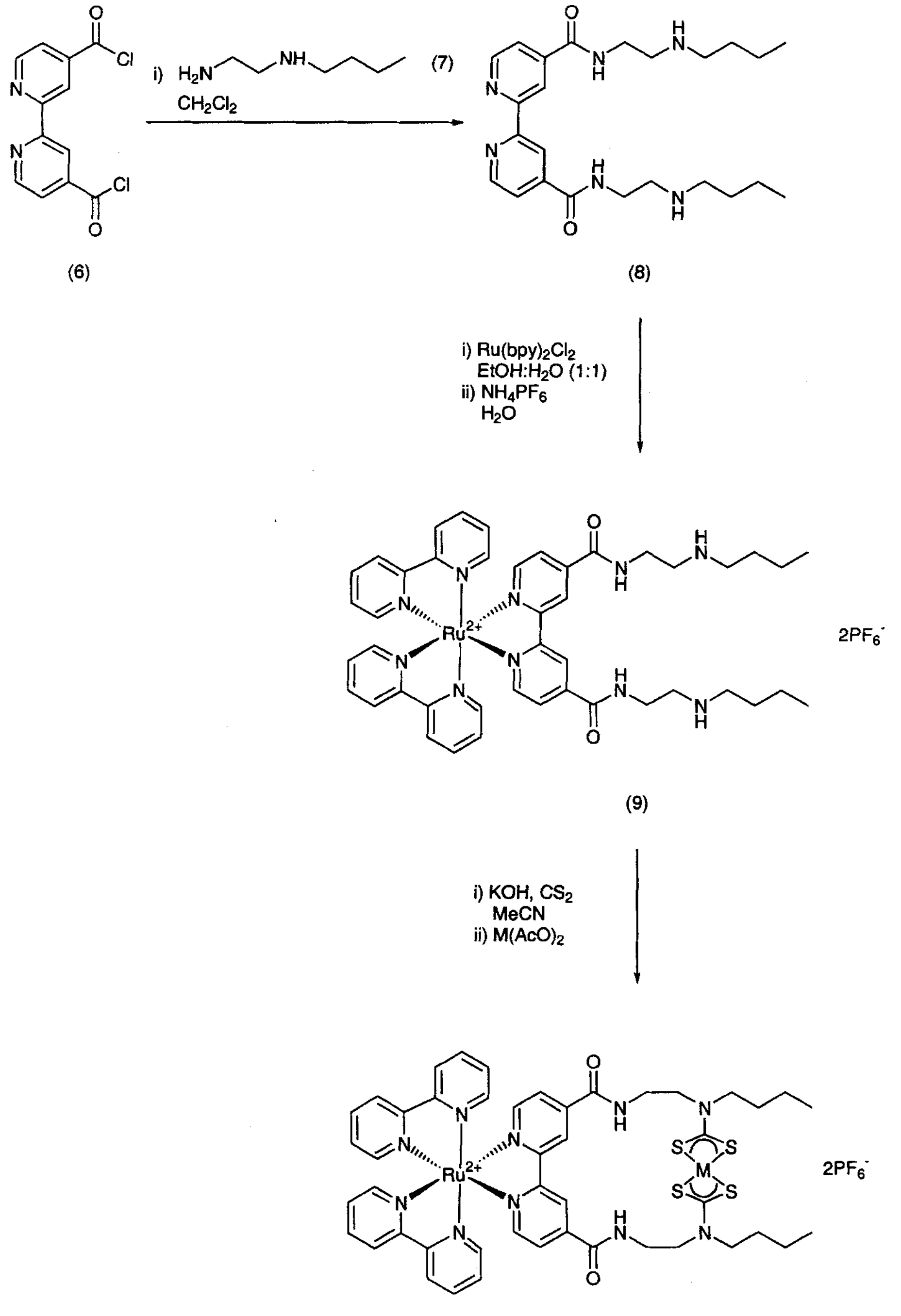
by hexylamine gave the thiourea-BOC derivative (**4**) in 83% yield. Deprotection with TFA, condensation with benzaldehyde and reduction with sodium borohydride afforded the secondary amine (**5**) in good yield. The addition of carbon disulfide, potassium hydroxide and nickel acetate produced L^4 as a green solid (Scheme 2).

The condensation of 4,4′-bis(chlorocarbonyl) 2,2′-bipyridine (**6**) with two equivalents of *N*-butylethylenediamine (**7**) gave the bipyridyl amide (**8**) in near quantitative yield. Addition of $(bipy)_2RuCl_2{\cdot}2H_2O$ in aqueous ethanol followed by excess NH_4PF_6 afforded the ruthenium(II) complex (**9**) which upon one-pot macrocyclisation with carbon disulphide, base and metal acetate gave the heterobimetallic receptors L^5, L^6 in good yield (Scheme 3). All these new receptors were characterised by ^1H NMR spectroscopy, electrospray mass spectrometry and elemental analysis.

The addition of tetrabutylammonium anion salts to DMSO-d_6 ^1H NMR solutions of L^1 and L^5 resulted in significant downfield perturbations of most notably the respective amide receptor protons by up to $\Delta\delta = 2.1$ ppm. With L^1 the resulting titration curves (Fig. 1) suggest the stoichiometry of anion binding is not simple and disappointingly the computer program EQNMR [20] could not determine stability constant values from this titration data. However 1:1 receptor: anion stability constant values were determined by EQNMR with L^5. Table I shows that compared

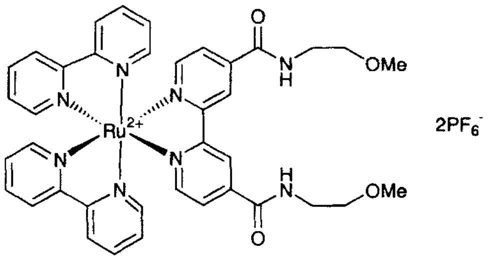


SCHEME 2



M = Ni (L^5), Zn (L^6)

SCHEME 3(1)



(L^7)
SCHEME 3(2)

with acyclic receptor, L^7, L^5 forms stronger complexes with Cl^- and OAc^- and displays the contrasting selectivity trend $Cl^- \sim AcO^- > Br^- \gg I^-$.

UV-visible anion titration experiments with L^1 and L^4 in 80% acetonitrile −20% DMSO solvent mixtures enabled stability constant values to be calculated using Specfit [21] and the results are summarised in Table II. Interestingly L^1 strongly complexes OAc^- with 1:1 stoichiometry whereas a $2A^-:L^1$ stoichiometric complex is formed with $H_2PO_4^-$. In contrast to L^5, these electronic spectral titration results suggest L^1 only weakly binds Cl^-. Table II reveals L^4, like L^1 forms strong complexes with carboxylate anions.

The electrochemical properties of L^2 were investigated because of solubility constraints in a 7:2:1 $CH_3CN:CH_2Cl_2$:DMSO solvent mixture using cyclic and square-wave voltammetry with Bu_4NBF_4 as the supporting electrolyte. L^2 exhibits a broad single quasi-reversible oxidation wave at $E_{pa} = 0.27\,V$, $E_{pc} = 0.04\,V$ (Table III) suggesting two overlapping waves. The addition of anions to electrochemical solutions of L^2 resulted in significant cathodic shifts of the copper(II)/copper(III) dithiocarbamate oxidation potential by up to $\Delta E = 160\,mV$ with $H_2PO_4^-$ (Table III). The complexed anion effectively stabilises the positively charged copper (III) centres facilitating the oxidation redox process.

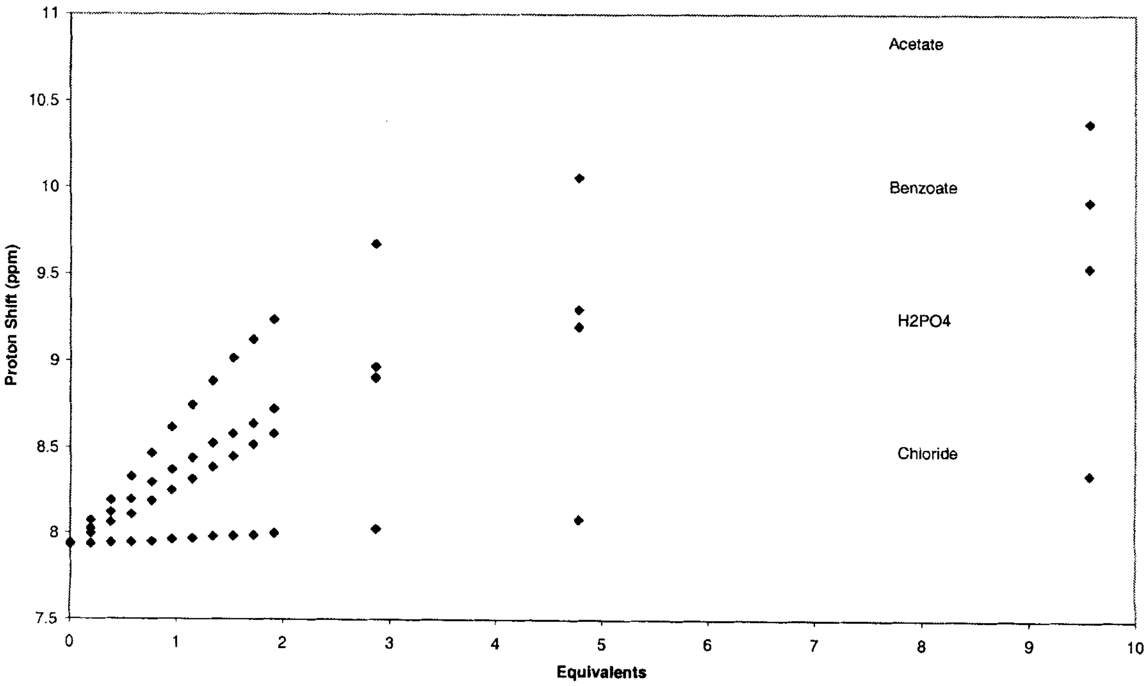


FIGURE 1 ^1H NMR binding curves for L^1 in DMSO.

TABLE I Stability constants (log β_1) (log β_1, the stability constant of the 1:1 complex) calculated from ^{1}H NMR titrations with (L^5) and (L^7) (errors <10%)

DMSO 293 K (K/dm^{3}mol^{-1})	Chloride	Bromide	Iodide	Acetate	$H_2PO_4^-$
L^5	3.01	2.28	0	3.00	*
L^7	2.18	–	–	2.54	–

* Precipitation occurred.

TABLE II Stability constants calculated from UV/Vis titrations with (L^1) and (L^4). To a host solution (2.5×10^{-6} mol dm^{-3}) was added aliquots of guest (2.5×10^{-3} mol dm^{-3}) as their tetrabutylammonium salts and the spectrum recorded immediately. log β_2 is the stability constant of the 2:1 (guest:host) complex

MeCN:DMSO (80:20) 25°C		Acetate	Benzoate	$H_2PO_4^-$	Chloride
L^1	log β_1	5.36 (0.06)*	†	4.10 (0.44)*	‡
	log β_2	–	–	9.07 (0.13)*	–
L^4	log β_1	6.13 (0.07)*	5.39 (0.05)*	†	‡

* Errors indicated in parentheses.
† Large change observed in the absorption spectrum upon anion addition, however a binding constant could not be calculated using Specfit.
‡ Little change observed in the absorption spectrum upon anion addition, suggesting weak binding.

TABLE III Electrochemical data for L^2 (MeCN:CH_2Cl_2:DMSO (70:20:10) as solvent. Obtained in a solution containing 0.1 mol dm^{-3} NBu_4BF_4 as supporting electrolyte. Solutions were 1×10^{-3} mol dm^{-3} in receptor and potentials were obtained with reference to Ag/Ag$^+$ electrode at 293 K, scan rate 100 mV s^{-1})

E_{pa} (V)	0.27
E_{pc} (V)	0.04
ΔE^* (mV) (Acetate)	70
ΔE^* (mV) (Benzoate)	120
ΔE^* (mV) ($H_2PO_4^-$)	160
ΔE^* (mV) (Cl^-)	130

* Cathodic shift of E_{pa} oxidation potential produced by the presence of 10 equivalents of anion added as their tetrabutylammonium salts.

In summary a series of new acyclic and macrocyclic transition metal dithiocarbamate based anion receptors containing amide and thiourea hydrogen bond donor groups have been prepared via metal mediated self-assembly. Preliminary anion coordination studies reveal even the neutral receptors L^1 and L^4 to strongly bind carboxylate and $H_2PO_4^-$ anions in competitive polar organic solvent mixtures. Electrochemical investigations show L^2 can electrochemically sense various anions via significant cathodic perturbations of the copper (II)/(III) dithiocarbamate redox couple.

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