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Metal-directed self-assembly of bimetallic dithiocarbamate transition metal cryptands and their binding capabilities†

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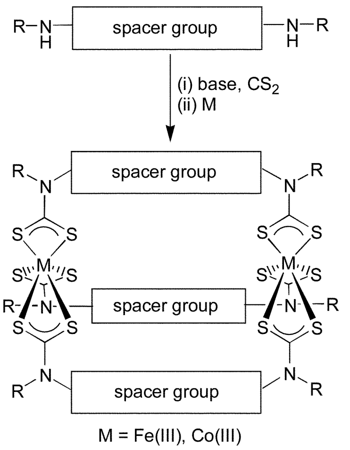
A novel family of redox-active dinuclear transition metal based cryptands self-assembled from dithiocarbamate ligands has been synthesised; depending upon the nature of the spacer groups these new cryptand systems have been shown to electrochemically recognise the binding of cations or anions.

The use of metal-directed self-assembly techniques provides a facile route to novel host macrocycles capable of binding charged and neutral guest substrates. Through careful consideration of ligand and preferred metal coordination geometry, among other factors, complicated and unusual molecular architectures are attainable.[1]

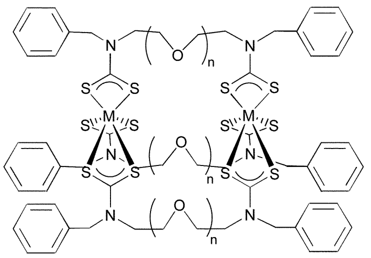
Recently the dithiocarbamate (dtc) moiety has proven to be a useful structural motif, lending itself to the metal-directed assembly of a range of structures including nano-sized resorcarene-based assemblies, catenanes, assorted macrocycles and trinuclear cages.[2] The incorporation of redox-active metal–ligand units into the framework of a host introduces the possibility of using the host as an electrochemical sensor for guest substrates.[3]

Herein, we describe the application of dithiocarbamate ligands for the first time in the construction of metal-directed self-assembled bimetallic cryptands. The cryptands can be assembled through careful choice of a suitable octahedral stereochemical directing metal centre such as Fe(III) and Co(III), as shown in Scheme 1. A range of redox-active metallo-cryptands with differing ligand spacer groups are presented, along with their preliminary electrochemical sensing results.

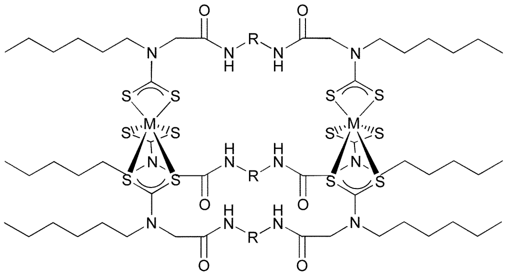
The starting secondary diamines containing polyether and alkyl–aryl amide linkages were prepared by straightforward synthetic methods.† Dithiocarbamate complexes were prepared in a one-pot synthesis from the parent secondary amines by reaction with carbon disulfide, base and an appropriate octahedral transition metal halide salt. The crude powders thus obtained were recrystallised to afford the analytically pure products **1–6** in yields of 13–76 %.



Scheme 1 General synthesis of dtc cryptands.



n = 1 | n = 2 | n = 3
1a M = Co(III) | **2a** M = Co(III) | **3a** M = Co(III)
1b M = Fe(III) | **2b** M = Fe(III) | **3b** M = Fe(III)



R = ethyl | R = *o*-phenyl | R = *m*-phenyl
4a M = Co(III) | **5a** M = Co(III) | **6a** M = Co(III)
4b M = Fe(III) | **5b** M = Fe(III) | **6b** M = Fe(III)

The new bimetallic cryptands **1–3** containing polyether cavities of various sizes were designed to complex and sense Group I metal cations. Initial evidence of metal cation binding was provided by electrospray mass spectrometry (ESMS) which revealed the formation of various alkali metal cation–cryptand complex adducts in the ESMS spectra. Proton NMR spectra of the diamagnetic cobalt(III) cryptands were too complicated to enable quantitative titration experiments to be carried out.

Electrochemical recognition studies were undertaken using cyclic and square wave voltammetry. The electrochemical properties of **1–3** differ to those of simple acyclic M(Et$_2$CNS$_2$)$_3$ complexes in exhibiting broad overlapping redox waves.

Table 1 Electrochemical Group I metal cation recognition data[a]

	ΔE_p/mV[b]			
	Li$^+$	Na$^+$	K$^+$	Cs$^+$
1a	20	25	15	5
2a	0	25	35	10
3a	0	20	30	45

[a] Square wave voltammograms recorded in 1 : 1 CH$_2$Cl$_2$–MeCN solutions containing 0.1 mol dm^{-3} NBu$_4$BF$_4$ as supporting electrolyte. [b] Anodic shift of the Co(IV)/Co(III) oxidation potential produced by presence of alkali metal cations (up to 5 equiv.) added as their perchlorate, hexafluorophosphate and triiodide salts.

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† Electronic supplementary information (ESI) available: selected experimental procedures. See http://www.rsc.org/suppdata/cc/b3/b308629a/

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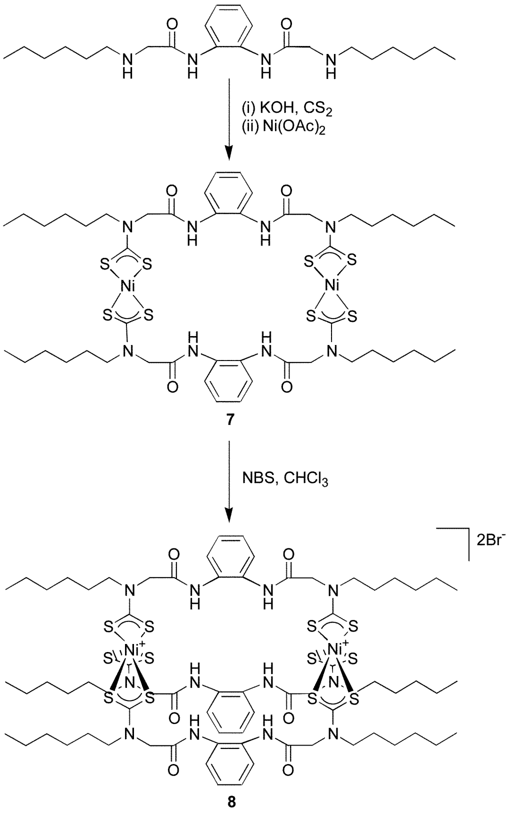
Table 2 Electrochemical anion recognition data[a]

	ΔE_p/mV[b]			
	Cl^-	OBz^-	HSO_4^-	$H_2PO_4^-$
5a	15	25	25	125
6a	60	50	50	90

[a] Square wave voltammograms recorded in CH_2Cl_2 solutions containing 0.1 mol dm^{-3} NBu_4BF_4 as supporting electrolyte. [b] Cathodic shift of the Co(IV)/Co(III) oxidation potential produced by presence of anions (up to 10 equiv.) added as their TBA salts.



Scheme 2 Synthesis of nickel(IV) cryptand **8**.

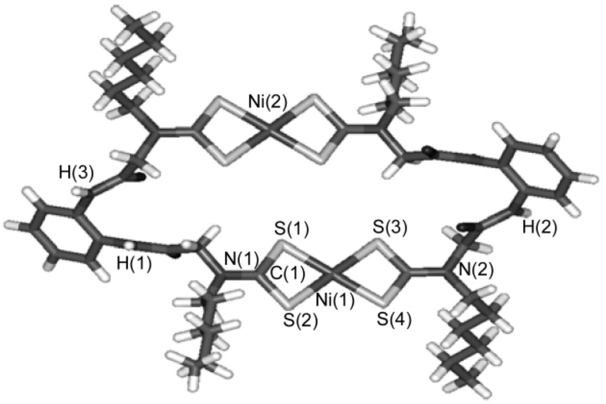


Fig. 1 Crystal structure of **7**.‡

Focusing on the irreversible Co(IV)/Co(III) oxidation redox couple of **1a, 2a** and **3a**, the addition of alkali metal cations led in most cases to significant anodic shifts where the cryptand-complexed metal cation destabilizes the cobalt(IV) oxidation state. It is noteworthy that Table 1 shows there is a correlation between magnitude of anodic shift and complementary metal cation : cryptand cavity size, and not as commonly observed with metal cation polarising character. For example with the large cryptand **3a**, Cs^+ causes the greatest perturbation of 45 mV whereas with the smaller cryptands **2a** and **1a**, K^+ and Na^+ respectively induce the largest anodic shifts. Electrochemical recognition experiments with $Co(Et_2CNS_2)_3$ revealed no evidence of interactions with Group I metal cations.[4]

With a view to constructing cryptands for anion complexation the new receptors **4–6** containing amide hydrogen bond donor groups were prepared using the one-pot synthetic protocol. Proton NMR anion titration experiments in polar organic solvents with the cobalt(III) cryptands proved problematic because of broadness of spectra. However, electrochemical anion binding studies revealed the respective Co(IV)/Co(III) redox couple to undergo significant cathodic perturbations of up to ΔE = 125 mV with $H_2PO_4^-$ in electrochemical dichloromethane solutions (Table 2). No anion induced shifts were seen with $Co(Et_2CNS_2)_3$.

An alternative method for bimetallic cryptand synthesis involving chemical oxidation of a preformed bimetallic nickel(II) dtc macrocycle was also investigated. Simple acyclic square planar nickel(II) $(dtc)_2$ complexes can undergo a two electron oxidation to form an octahedral nickel(IV) $(dtc)_3$ positively charged species.[5]

The new bimetallic nickel(II) macrocycle **7** was initially synthesised in 76% yield (Scheme 2). Crystals of **7** were grown from a chloroform–acetonitrile solution, and the structure is shown in Fig. 1. As expected the nickel(II) dithiocarbamate group forms an almost square planar linkage[6] with the nickel atom lying only 3.2° out of the plane. The macrocycle **7** was oxidised using two equivalents of *N*-bromosuccinimide (NBS) in $CHCl_3$ to produce the novel bimetallic Ni(IV) cryptand **8** which was characterised by UV/visible spectroscopy, electrochemistry, infrared, electrospray mass spectrometry (ESMS) and elemental analysis (Scheme 2). Preliminary anion binding studies in $CHCl_3$–MeCN (4 : 1) revealed the addition of chloride and nitrate anions to **8** produced cathodic shifts of the Ni(IV)/Ni(III) wave of 70 mV and 15 mV respectively.

In conclusion, the dithiocarbamate ligand system has proven its versatility in providing a route to the metal-directed self-assembly of a range of novel bimetallic cryptands containing octahedral metal ions. Initial binding studies show these systems are useful in the electrochemical sensing of cations and anions.

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Notes and references

‡ Crystal data for $C_{50}H_{71}N_9Ni_2O_4S_8$, M = 1236.08, monoclinic, a = 34.0525(6), b = 19.3859(4), c = 9.4251(2) Å, β = 102.058(3)°, V = 6084.6 Å^3, T = 150 K, space group $C\,2/c$, Z = 4, 45757 reflections measured, 7118 unique (R_{int} = 0.057) were used in all calculations. The final $R1$ (all data) was 0.0457 and $wR2$ (all data) was 0.0524. CCDC 216372. See http://www.rsc.org/suppdata/cc/b3/b308629a/ for crystallographic data in .cif or other electronic format.

1 R. W. Saalfrank and I. Bernt, *Curr. Opin. Solid State Mater. Sci.*, 1998, **3**, 407; M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289.

2 O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 136; M. E. Padilla-Tosta, O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 4235; P. D. Beer, N. Berry, M. G. B. Drew, O. D. Fox, M. E. Padilla-Tosta and S. Patell, *Chem. Commun.*, 2001, 199; P. D. Beer, A. G. Cheetham, M. G. B. Drew, O. D. Fox, E. J. Hayes and T. D. Rolls, *Dalton Trans.*, 2003, **4**, 603.

3 P. D. Beer, P. A. Gale and G. Z. Chen, *Coord. Chem. Rev.*, 1999, **185**, 3.

4 Preliminary electrochemical Group I metal cation binding studies with the Fe(III) polyether cryptands revealed insignificant perturbations of the Fe(IV)/(III) redox couples.

5 J. P. Fackler Jr., A. Avdeef and R. G. Fischer Jr., *J. Am. Chem. Soc.*, 1973, **95**, 774.

6 M. Bonamico, G. Dessy, C. Mariani, A. Vaciago and L. Zambonelli, *Acta Crystallogr.*, 1965, **19**, 619; M. N. I. Khan, J. P. Fackler Jr., H. H. Murray, D. D. Heinrich and C. Campana, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1987, **43**, 1917.