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Self-assembled dithiocarbamate–copper(II) macrocycles for electrochemical anion recognition†

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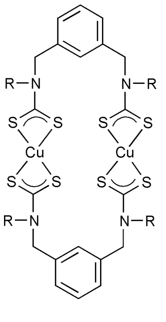
A novel family of redox-active dinuclear copper(II)-based macrocycles self-assembled from dithiocarbamate ligands has been synthesised; a naphthyl-spaced complex exhibits selective electrochemical recognition of perrhenate and dihydrogenphosphate anions.

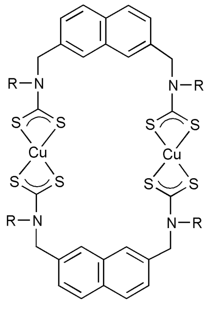
The use of metal-directed self-assembly techniques provides a facile route to novel host macrocycles capable of binding charged and neutral guest substrates.[1,2] In some instances macrocycle formation can be templated by the guest and therefore the size and stability of the assembly is promoted by the complementarity between host and guest.[3]

We recently demonstrated the utility of the dithiocarbamate (dtc) moiety as a coordinating group[4] in the transition metal-directed construction of nano-sized resorcarene-based assemblies.[5] The incorporation of redox-active metal–ligand units into the macrocycle framework of a host introduces the possibility of using the host as an electrochemical sensor for guest substrates.[6] Herein, we describe the application of dithiocarbamate ligands in the construction of metal-directed self-assembled macrocycles. A range of copper-based, redox-active metallomacrocycles, their structural characterisation and preliminary electrochemical anion sensing results are presented.

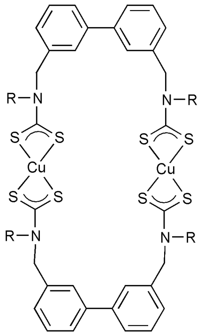
The starting diamines were simply prepared by reaction of the appropriate bis(bromomethyl)aromatic compound with neat alkylamine. Dithiocarbamate copper(II) macrocycles were prepared in a one-pot synthesis from the parent secondary amines by reaction with carbon disulfide, potassium hydroxide and copper(II) acetate. The crude powders were recrystallised from dichloromethane–ethanol mixtures to afford the analytically pure metallomacrocycles **1–7** in yields of 40–70%.



R
n-propyl **1**
n-butyl **2**
n-hexyl **3**



R
n-butyl **4**
n-hexyl **5**



R
n-propyl **6**
n-butyl **7**

Electrospray mass spectrometry (ESMS) in pure methanol solutions confirmed the presence of all dinuclear macrocyclic structures. Treatment of copper(II) macrocycle **1** with iron(III) chloride gave upon crystallisation the complex $[Cu_2L_2][FeCl_4]_2$ **8**.[7] The structure of **8** was characterised by X-ray crystallography‡ and is shown in Fig. 1. There is only one crystallographically unique copper(III) ion present, a centre of inversion relating the two copper ions. The copper–copper distance in **8** is quite short at 5.5 Å. In profile, the structure of **8** forms a step-like structure, the two aromatic phenyl groups remaining planar and the two dtc–Cu–dtc moieties twisting out of the plane at an angle to the plane of the aromatic rings. There are two tetrachloroferrate(III) anions associated with each macrocycle and each exhibits a single axial interaction *via* a chlorine atom to a copper(III) centre, Cu–Cl 3.00 Å. The nature of this solid-state association led us to consider the possibility of anion interactions with the oxidized macrocycles.

The electrochemical properties of the copper(II) metallomacrocycles **2**, **4** and **7** were investigated in CH_2Cl_2–MeCN (4 : 1) using cyclic and square-wave voltammetry with NBu_4BF_4 as the supporting electrolyte. The xylyl-spaced complex **2** exhibits two quasi-reversible oxidation waves at 0.06 and 0.20 V [Table 1 and Fig. 2(a)]. The observation of two oxidation potentials indicates either electrochemical coupling between the two proximal copper centres or that in solution the two copper centres are in different coordination environments. The naphthyl-spaced complex **4**, with more separated copper centres, exhibits a single, broad, quasi-reversible oxidation wave at 0.19 V suggesting two overlapping waves [Fig. 2(b)]. However interestingly, the biphenyl-spaced copper(II) complex **7** again exhibits two distinct reversible oxidation waves at 0.04 and 0.19 V respectively even though molecular models predict that this complex possesses the longest Cu···Cu distance [Fig. 2(c)].

The copper(II)/(III) redox couples of macrocycles **2**, **4** and **7** in the presence of anions (ReO_4^-, $H_2PO_4^-$, Cl^-, Br^-, NO_3^-) (Table 1) were investigated by square-wave and cyclic voltammetry. Notably, substantial cathodic shifts in oxidation potential are seen for naphthyl-based macrocycle **4** with tetrahedral anions such as dihydrogenphosphate and per-

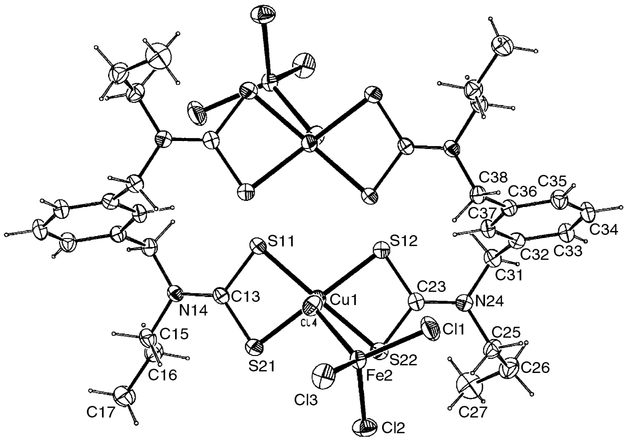


Fig. 1 Structure of the copper(III) complex **8** with associated $FeCl_4^-$ anions; ellipsoids at 20% probability.

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† Electronic supplementary information (ESI) available: diamine structures, experimental and characterisation data. See http://www.rsc.org/suppdata/cc/b0/b007296f/

Table 1 Electrochemical data[a]

	Receptor		
	2	**4**	**7**
$E_{½}$/V	0.06 0.20	0.19[b]	0.04 0.19
ΔE (Cl$^-$)[c]/mV	20	< 10	< 10
ΔE (NO$_3^-$)[c]/mV	< 10	< 10	< 10
ΔE (Br$^-$)[c]/mV	< 10	< 10	< 10
ΔE (ReO$_4^-$)[c]/mV	< 10	85	< 10
ΔE (H$_2$PO$_4^-$)[c]/mV	< 10	85	< 10

[a] Obtained in CH_2Cl_2–MeCN (4 : 1) solution containing 0.2 mol dm^{-3} NBu_4BF_4 as supporting electrolyte. Solutions were *ca.* 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}. [b] Broad quasi-reversible oxidation wave: E_{pa} = 0.25 V, E_{pc} = 0.11 V, suggesting two overlapping waves. [c] Cathodic shift of $E_{½}$ oxidation potential produced by presence of 5 equiv. of anion added as their NBu_4^+ salts.

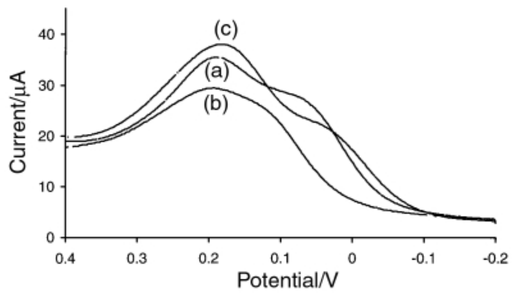

Fig. 2 Square-wave voltammograms of (a) **2**, (b) **4** and (c) **7** in CH_2Cl_2–MeCN (1 : 1), NBu_4BF_4 supporting electrolyte, Ref: Ag/AgCl.

rhenate.[8] For example with **4** the addition of five equivalents of tetrabutylammoniumperrhenate gave a cathodic shift of 85 mV in the Cu(II)/Cu(III) redox couple (see Fig. 3). The complexed anion effectively stabilises the copper(III) oxidation state. Interestingly no significant perturbations were observed with chloride, bromide or nitrate anions. In contrast the smaller xylyl-spaced macrocycle exhibits a noticeable cathodic perturbation to chloride (20 mV) but little response to nitrate, bromide or the larger anions such as perrhenate or dihydrogenphosphate. For the control bis(diethyldithiocarbamate)copper(II) a single quasi-reversible oxidation wave at 0.07 V is observed which exhibits no significant perturbations in oxidation potential on the addition of anions.

The interaction of **4** with perrhenate was investigated further by UV–VIS spectroscopy. Solutions of **2**, **4** and **7** in CH_2Cl_2–MeCN (0.1 M NBu_4BF_4) were oxidised with $NOBF_4$ to the corresponding dicationic copper(III) complexes.§ On addition of 5 equiv. of NBu_4ReO_4 to freshly prepared $[\mathbf{4}]^{2+}$ (λ_{max} = 421 nm) a bathochromic shift of 10 nm was observed in the maximum absorption. However, no such shifts were observed on the addition of NBu_4ReO_4 to $[\mathbf{2}]^{2+}$, $[\mathbf{7}]^{2+}$ or the oxidised monocation of bis(diethyldithiocarbamate)copper(II).¶ Further evidence for the interaction of $[\mathbf{4}]^{2+}$ with ReO_4^- came from ES-MS studies.[9] Oxidation of copper(II) macrocycles in acetonitrile–dichloromethane mixtures with copper(II) triflate, perchlorate or tetrafluoroborate gave in all cases the doubly oxidised species, $[Cu_2L_2]^{2+}$ of the copper(III) macrocycles (L = ligand). Addition of ReO_4^- anions to solutions of macrocycle **4** oxidised with copper(II) triflate or tetrafluoroborate gave the ion corresponding to the doubly oxidised species $[Cu_2L_2][ReO_4]^+$, 1275.2.‖ This species was predominant even in the presence of a large excess of tetrafluoroborate anion. Space filling molecular models indicate anions such as ReO_4^- and $H_2PO_4^-$ may comfortably occupy the cavity and bridge the copper centres in **4**, but are too large for the xylyl-spaced **2** and too small for biphenyl-spaced **7**. This suggests this macrocyclic system may exhibit a measure of anion selectivity based upon the macrocycle ring size.[10]

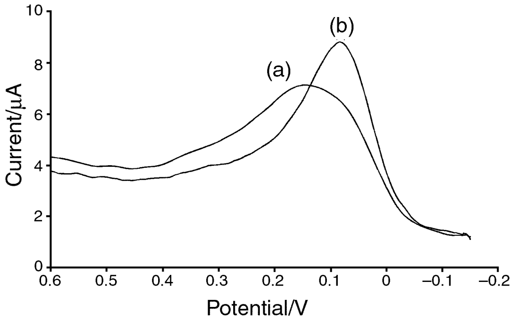

Fig. 3 Square-wave voltammograms of (a) **4** and (b) **4** plus 5 equiv. of NBu_4ReO_4; in CH_2Cl_2–MeCN (1 : 1), NBu_4BF_4 supporting electrolyte, Ref: Ag/AgCl.

In summary, copper(II) metallomacrocycles **1**–**7** are novel examples of redox-active macrocyclic hosts whose oxidation states and hence binding affinities can be chemically switched by redox control. In addition we have demonstrated the use of the dtc–copper(II)/(III) redox couple as an electrochemical anion-sensing unit. These preliminary electrochemical sensing results suggest anion selectivity is dictated by the size of dithiocarbamate copper(II) macrocycle.

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Notes and references

‡ *Crystal data* for $[Cu_2L_2][FeCl_4]_2$ **8**: $C_{42}H_{56}Cl_8Cu_2Fe_2N_4S_8$, M_r = 1419.78, triclinic, space group $P\bar{1}$, Z = 1, a = 10.751(12), b = 12.229(14), c = 12.598(14) Å, α = 95.657(10), β = 107.331(10), γ = 98.744(10)°, U = 1544 Å^3, D_c = 1.526 g cm^{-3}, μ = 1.76 mm^{-1}, 5535 unique data.

CCDC 182/1869. See http://www.rsc.org/suppdata/cc/b0/b007296f/ for crystallographic files in .cif format.

§ **2**: Cu(II) λ_{max} = 432, Cu(III) λ_{max} = 416; **4**: Cu(II) λ_{max} = 433, Cu(III) λ_{max} = 421; **7**: Cu(II) λ_{max} = 440, Cu(III) λ_{max} = 431; bis(diethyldithiocarbamate)copper(II): Cu(II) λ_{max} = 434, Cu(III) λ_{max} = 425 nm.

¶ UV–VIS spectroscopic anion titrations with the neutral receptors gave no evidence of anion binding. Preliminary UV–VIS titrations of $[\mathbf{4}]^{2+}$ with NBu_4ReO_4 gave a stoichiometry of 1 : 2 receptor : anion.

‖ Under the same conditions oxidized receptors **2** and **7** gave only very weak peaks for adducts with ReO_4^-.

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