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Communication

Metal-directed assembly of polyferrocenyl transition metal dithiocarbamate macrocyclic molecular boxes

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Abstract

Novel redox-active polyferrocenyl transition metal dithiocarbamate macrocyclic molecular boxes (**10a**–**c**), (**11**) and (**12a**–**c**) are synthesised by reaction of the respective ferrocenyl secondary amines, namely, *N*,*N*′-bis(ferrocenemethyl)-1,3-bis(aminomethyl)-benzene (**4**), 1,1′-bis(benzylaminomethyl)ferrocene (**8**) and 1,1′-bis((ferrocenylmethyl)aminomethyl)ferrocene (**9**) with carbon disulfide, potassium hydroxide and transition metal (zinc, copper, nickel) acetate in high yields (52–82%) and characterised by spectroscopic and electrochemical techniques. The single-crystal X-ray structure of **10a** shows that each zinc atom is in tetrahedral geometry, being bonded to two dithiocarbamate ligands with Zn–S distances 2.32(1)–2.44(1) Å. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metal-directed assembly; Macrocyclic molecular boxes; Ferrocenyl amines

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Metal-directed self-assembly of two- and three-dimensional macrocyclic and cage-like receptors is currently an area of intense research activity [1,2]. By judicious choice of metal ion and multidentate ligand components, the resulting self-assembled polymetallic hosts can exhibit unique electronic and magnetic properties and have the potential to bind guest substrates [3]. To date, the majority of metal-directed assemblies reported are based on pyridyl derivatised ligands and use metal ions in diamagnetic valent states, notably palladium and platinum. Using the dithiocarbamate ligand [4] as a self-assembling construction motif for the first time, we have recently synthesised novel nano-sized resorcarene-based transition metal polymetallic assemblies [5] and copper(II)-dithiocarbamate macrocycles [6]. The incorporation of redox-active components such as ferrocene into a macrocyclic ligand framework introduces the possibility of the host being capable of electrochemically recognising guest species [7]. We report here, the zinc, copper and nickel metal-directed syntheses of novel redox-active polyferrocenyl transition metal dithiocarbamate macrocyclic molecular boxes including the single-crystal X-ray structure of a bis-zinc-dithiocarbamate ferrocenyl macrocycle.

The redox-active ferrocene moiety was incorporated into the target molecular boxes on the periphery and/or as part of the macrocyclic structural framework via initial preparation of ferrocenyl secondary amines. Schiff base condensation of two equivalents of ferrocenecarboxaldehyde (**1**) with 1,3-diaminomethylbenzene (**2**) under melt conditions gave the bis-imine intermediate (**3**), which on reduction with sodium borohydride produced the diamine (**4**) in good overall yield (Scheme 1). Analogous solution Schiff base condensation reactions of 1,1′-bis(carboxaldehyde) ferrocene (**5**) [8] with two equivalents of benzylamine (**6**) and ferrocenemethylamine (**7**) followed by sodium borohydride reduction gave the ferrocenyl secondary amines (**8**) and (**9**) in 70 and 89% yields, respectively (Schemes 2 and 3).

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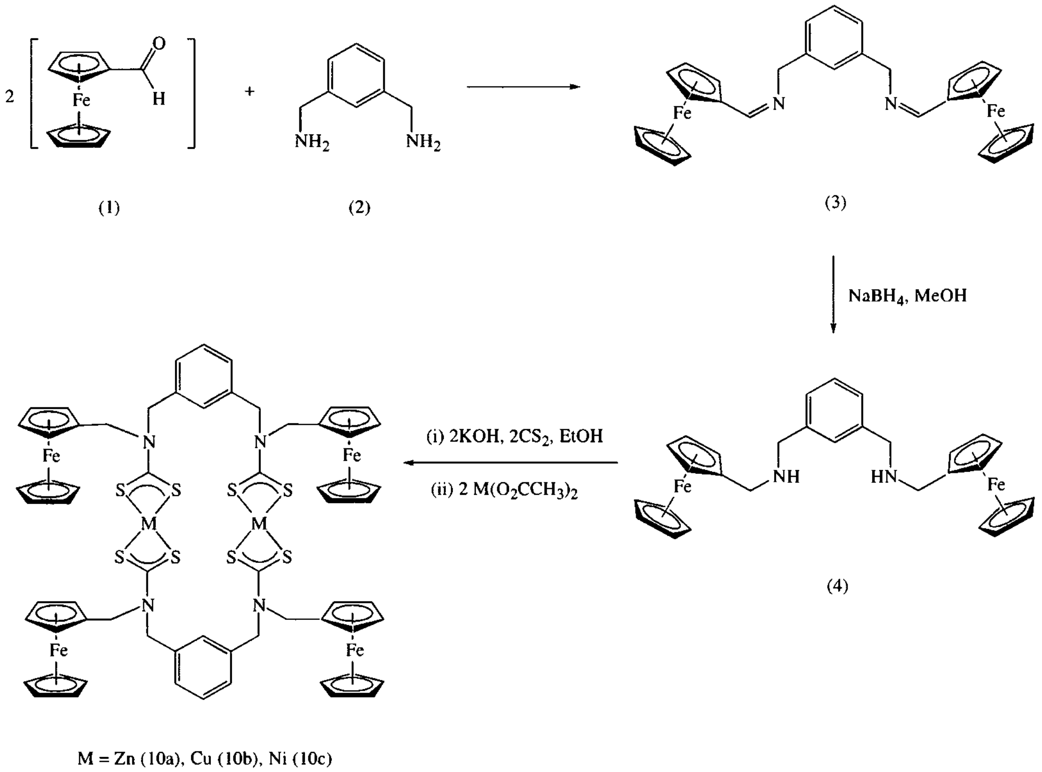
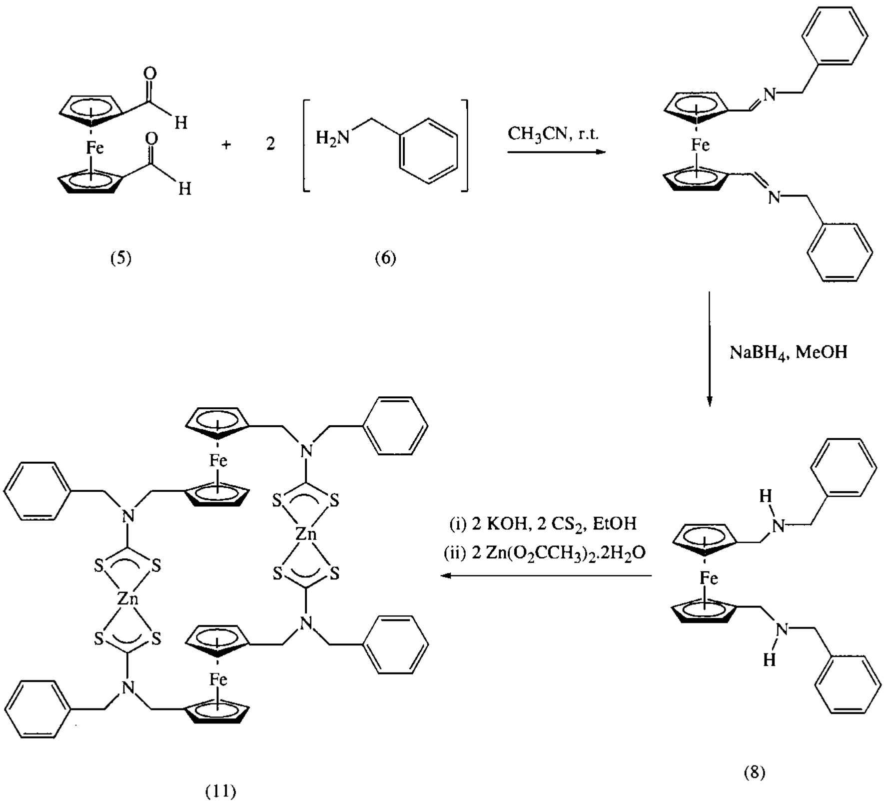
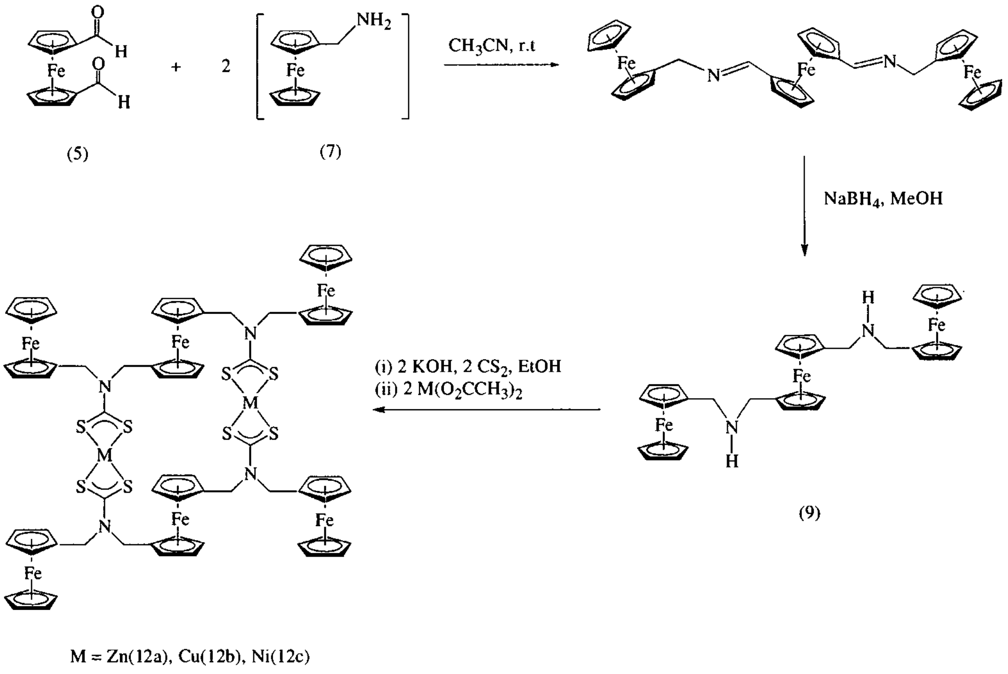


Scheme 1.



Scheme 2.



Scheme 3.

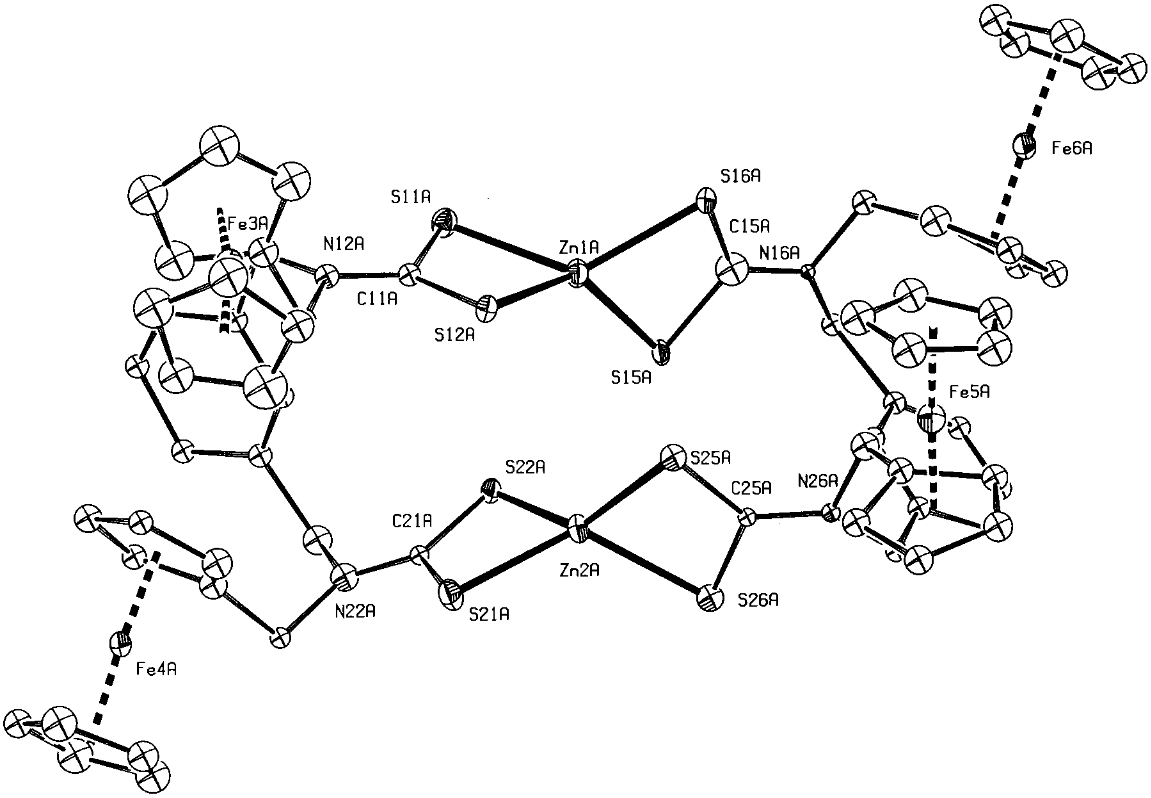


Fig. 1. The structure of **10a** with ellipsoids at 15% probability. The two molecules in the asymmetric unit have equivalent geometries. Hydrogens atoms are omitted for clarity.

Dithiocarbamate zinc(II), copper(II) and nickel(II) ferrocenyl-containing macrocyclic molecular boxes (**10a**–**c**), (**11**) and (**12a**–**c**) were prepared in a one-pot metal-directed self-assembly synthesis by reaction of the appropriate ferrocenyl secondary amine with carbon disulfide, potassium hydroxide and metal acetate in yields of 52–82% (Schemes 1–3). All these new polyferrocenyl transition metal dithiocarbamate macrocyclic molecular boxes were characterised by ^{1}H-NMR spectroscopy (for diamagnetic boxes),

Table 1
Electrochemical data

Complex	$E_{1/2}$ (V)
10a	0.25
10b	0.26 [a]
10c	0.26, 0.31 [b]
11	0.35
12a	0.24, 0.34 [b]

Obtained in CH_2Cl_2–CH_3CN 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 complex and potentials were obtained with reference to Ag | Ag^+ electrode at 293 K, scan rate = 100mV s^{-1}.

[a] Broad oxidation wave suggesting two overlapping waves.

[b] Irreversible oxidation, E_{pa} value quoted.

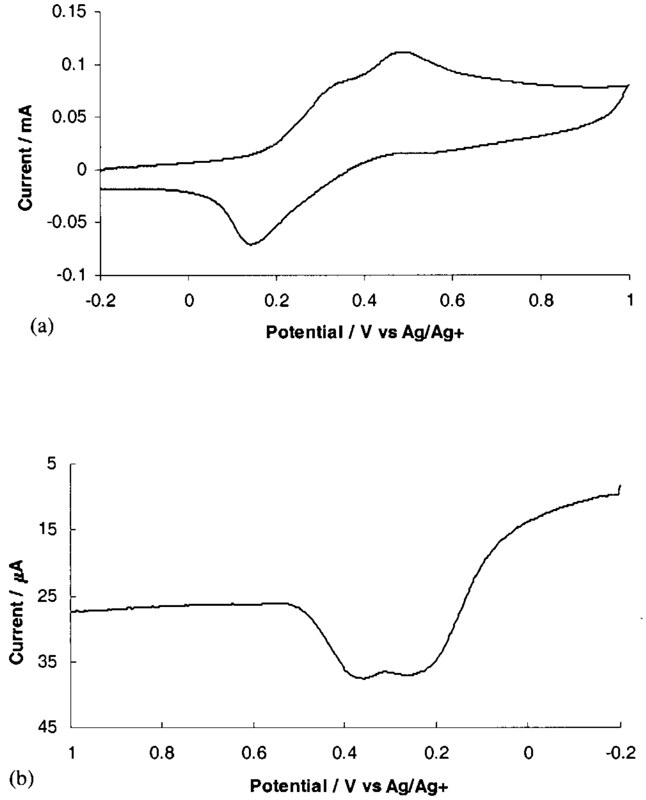


Fig. 2. (a) Cyclic-and (b) square wave voltammograms of **12a**.

electrospray/FAB mass spectrometry and elemental analysis.

The structure of **10a** was characterised by X-ray crystallography.[1] The two molecules in the asymmetric unit have equivalent geometries and the structure of one molecule is shown in Fig. 1. Each zinc atom is four-coordinate, being bonded to two dithiocarbamate ligands with Zn–S distances 2.32(1)–2.44(1) Å. Allowing for the distortions caused by the chelating four-membered ring, the metal environment can be considered as tetrahedral although the two chelate rings are not perpendicular with intersection angles ranging from 79.5(2)–81.2(2)°.

In the two independent binuclear molecules, the Zn...Zn distances are 4.09(1), 4.10(1) Å, respectively. Fe–C distances in the cyclopentadiene moieties range from 1.89(2)–2.23(2) Å. The remaining dimensions in the two molecules are as expected.

The electrochemical properties of (**10a**–**c**), (**11**) and (**12a**) were investigated by cyclic- and square wave voltammetry in a 4:1 dichloromethane–acetonitrile solvent mixture with tetrabutylammonium tetrafluoroborate as the supporting electrolyte (Table 1). The bis-zinc xylyl-bridged dithiocarbamate dimer (**10a**) containing four redox-active ferrocenyl groups on the macrocycle periphery exhibits a single reversible oxidation wave at $E_{1/2} = 0.25$ V which suggests that all four ferrocene moieties are oxidised in a single step and are electrochemically independent of one another. The bis-copper(II) analogue (**10b**) displays a broad oxidation redox wave at ca. $E_{1/2} = 0.26$ V, which taking into account the electrochemical properties of $Cu[Et_2NCS_2]_2$ [9] suggests that the copper(II)/copper(III) dithiocarbamate redox couple overlaps with the respective ferrocene oxidation couple. With the bis-nickel(II) macrocycle (**10c**), two oxidation couples are observed, a reversible wave at $E_{1/2} = 0.26$ V which corresponds to the ferrocene redox couple, and an irreversible oxidation at $E_{pa} = 0.31$ V assignable to the known Ni(II)/Ni(IV) dithiocarbamate [9] oxidation process. The two ferrocenyl spacer moieties of the macrocyclic zinc(II) molecular box (**11**) are reversibly oxidised in a single step at $E_{1/2} = 0.35$ V and the zinc(II) macrocycle (**12a**) containing six ferrocene groups displays two oxidation waves, but only one return reduction wave is observed (Fig. 2a). Studies are in progress to delineate this more complicated electrochemical behaviour.

In summary, using metal-directed self-assembly, a series of novel redox-active polyferrocenyl transition

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[1] *Crystal data*: $C_{66}H_{67}Fe_4N_4O_{1.5}S_8Zn_2$, $M = 1550.85$, monoclinic, spacegroup *Cc*, $Z = 8$, $a = 15.30(2)$, $b = 30.25(3)$, $c = 32.34(4)$ Å, $\beta = 102.58(1)°$, $U = 14614$ Å^3, dm = 1.410 gm cm^{-3}, $\mu = 1.690$ mm^{-1}. 16893 independent reflections ($R_{int} = 0.0990$) were collected on a Marresearch image plate system. The crystal was positioned at 70 mm from the image plate. 100 frames were measured at 2° intervals with a counting time of 10 min. Data analysis was carried out with the XDS program [10]. The structure was solved using direct methods with the SHELX 86 program [11]. There are two molecules in the asymmetric unit. Zn, Fe and S atoms were refined anisotropically while other atoms were refined isotropically. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they were attached. Because of the poor quality of the data, a consequence of abnormal spot shapes, 40 distance and thermal constraints were necessary. Solvent molecules included four ethanol molecules all with 50% occupancy and two water molecules also with 50% occupancy. An empirical absorption correction was applied with DIFABS [12]. The structure was refined on F^2 using SHELXL [13]. The final *R* values were *R*1 0.1236, *wR*2 0.2941 for 5886 data with $I > 2\sigma(I)$.

metal dithiocarbamate macrocyclic molecular boxes have been prepared and characterised by spectroscopic and electrochemical techniques.

1. Experimental

10a. To an EtOH (30 ml) solution of *N*,*N*′-bis(ferrocenemethyl)-1,3-bis(aminomethyl)benzene (**4**) (1.00 g, 1.88 mmol) and KOH (0.23 g, 4.10 mmol), was added CS_2 (0.32 g, 4.20 mmol) and the solution was stirred for 2 h. Zinc(II) acetate hydrate (0.41 g, 1.88 mmol) was added and the mixture was stirred for 12 h. The resulting creamy-orange precipitate was filtered, collected and recrystallised from a CH_2Cl_2–*n*-hexane solvent mixture. Yield: 0.96 g, 68%. Anal. Found: C, 51.05; H, 3.81; N, 3.75. Calc. for $C_{64}H_{60}N_4S_8Fe_4Zn_2$: C, 51.39; H, 4.04; N, 3.75%. ESMS; (MeOH/1% HCOOH) m/z: 1496 $[M + H^+]$. ^{1}H-NMR (DMSO-d_6): δ 4.16 (s, 20H, C_5H_5), 4.17 (t, 8H, σ-C_5H_4), 4.43 (t, 8H, m-C_5H_4), 4.85 (s, 8H, $C_5H_4CH_2$), 5.08 (s, 8H, $C_6H_4CH_2$), 7.29–7.41 (m, 8H, C_6H_4). ^{13}C-NMR (DMSO-d_6): δ 205.3 (CS_2), 136.1 (Aryl CC), 129.0 (Aryl CH), 127.3 (Aryl CH), 126.7 (Aryl CH), 81.5 (Ferrocenyl CC), 70.0 (Ferrocenyl CH), 68.6 (Ferrocenyl CH), 68.3 (Ferrocenyl CH), 55.7 ($C_6H_4CH_2$), 52.6 ($C_5H_4CH_2$).

2. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157125 for $C_{66}H_{67}Fe_4N_4O_{1.5}S_8Zn_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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