

New Polyaza Tris-ferrocene and Tris-2,2'-bipyridyl Macrobicyclic Cryptand Molecules. Isolation of Homo- and Hetero-polymetallic Zinc(II) and Copper(I) Cryptates containing Externally Coordinated Ruthenium(II) Cations

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New multisite ligands containing either three peripherally linked ferrocene redox centres (L¹, L³) or three externally orientated 2,2'-bipyridyl transition metal recognition sites (L², L⁴) have been prepared and their homo- and hetero-polymetallic zinc(II) and copper(I) cryptates incorporating in the case of L² and L⁴ externally coordinated ruthenium(II) cations have been isolated.

The design and synthesis of polytopic macrocyclic and macrobicyclic ligands containing recognition sites for binding several guest species is of considerable current interest.¹⁻⁷ Such receptors are able to form polynuclear metal complexes which in some instances have been shown to exhibit novel allosteric,^{8,9} cooperative and catalytic properties. In particular, dinucleating macrobicyclic ligands capable of simultaneously binding two metal ions in close proximity to one another have the ability subsequently to complex substrate species between the bound metal cations to produce 'cascade' complexes.¹⁰

We are currently interested in fabricating new multisite ligands that contain multiple metallocene redox-active groups¹¹ and/or *external* transition metal recognition sites such as bipyridyl¹² as part of macrocyclic host structural frameworks. We report here the syntheses, preliminary coordination and electrochemical studies of a number of new macrobicyclic ligands which contain these novel features. We also demonstrate that the new macrobicyclic cryptand receptors can form a variety of heteropolymetallic complexes through external and/or internal cryptate complex formation with ruthenium(II), copper(I) and zinc(II) guest cations.

Ferrocene-1,1'-dicarbaldehyde **1**¹³ was prepared *via* a new one-pot procedure from the dilithioferrocene-*N,N,N',N'*-tetramethylethylenediamine (tmeda) complex and dimethylformamide.¹⁴ The crude product was purified by flash chromatography on silica gel to give **1** in yields of up to 80%. This vital synthon can be used to synthesise a variety of novel macrobicyclic Schiff base ligands *via* condensation with appropriate di- or tri-amines.

The new Schiff base cryptands L¹ and L² were prepared by adaptation of the recently developed one-step synthetic methodology of tripodal (2 + 3) condensation of an appropriate dialdehyde with tris-(2-aminoethyl)amine **2**.¹⁵ Reaction of three moles of **1** and 4,4'-diformyl-2,2'-bipyridyl **3**,

prepared *via* Swern oxidation of the corresponding dialcohol in 75% yield, with two moles of tris-(2-aminoethylamine) **2** in dry acetonitrile solution gave L¹ and L² in 85 and 70% yields respectively (Schemes 1 and 2). These Schiff base cryptands were easily reduced using NaBH₄ to give the octaaza derivatives L³ and L⁴ in 78 and 92% yields respectively. The structures of all these new ligands were characterised on the basis of spectroscopic and analytical evidence.†

The new cryptand ligands are all polytopic in design and in the case of L² and L⁴ contain internal *and* external recognition sites for binding transition metal guest cations.

The addition of two equivalents of Zn(dmsO)₅(ClO₄)₂ to respective dimethyl sulphoxide (dmsO) solutions of L¹ and L³ led to the isolation of the dinuclear cryptates [L¹Zn₂](ClO₄)₄ **4** and [L³Zn₂](ClO₄)₄ in excellent yields.‡ Disappointingly cyclic voltammetric experiments in dmsO revealed the respec-

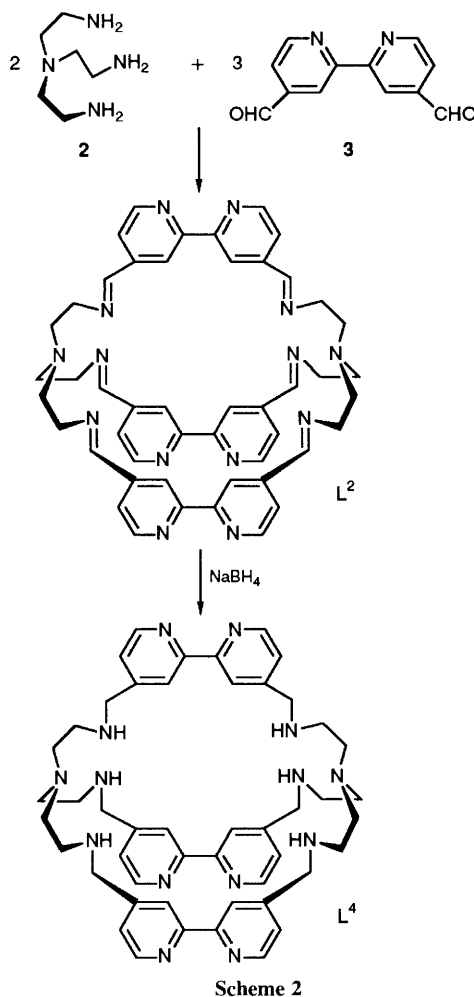
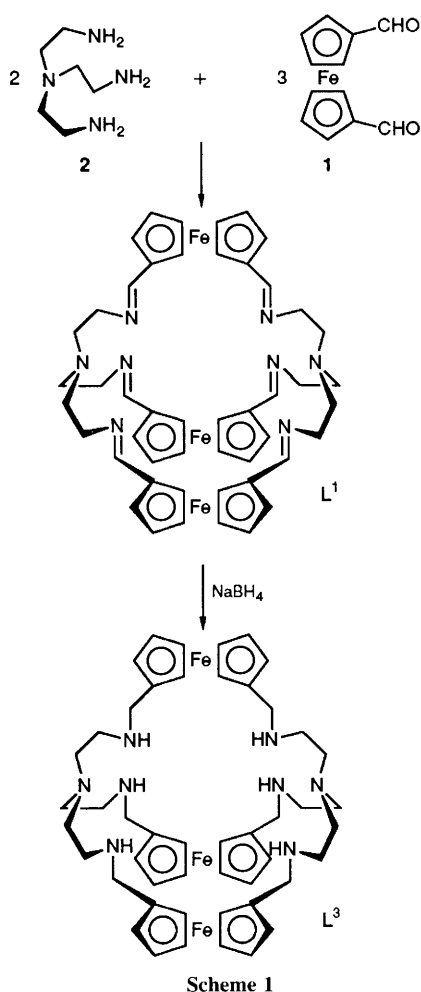
† All new compounds gave spectroscopic and analytical data in accordance with assigned structures. Data are quoted for a selection of the ligands. For L¹ (Found: C, 63.0; H, 6.2; N, 12.15. C₄₈H₅₄N₈Fe₃ requires C, 63.3; H, 6.0; N, 12.3%; *m/z* (FAB) 911 (M + H)⁺; δ_H (400 MHz, CDCl₃) 2.70–2.93 (m, 12H, CH₂), 3.51–3.67 (m, 12H, CH₂N=), 4.25–4.44 (m, 12H, FeH), 4.58–4.75 (m, 12H, FeH), 7.88 (s, 3H, CH=N) and 8.10 (s, 3H, CH=N).

For L² (Found: C, 68.9; H, 6.0; N, 23.3. C₄₈H₄₈N₁₄·H₂O requires C, 68.7; H, 6.0; N, 23.4%; *m/z* (FAB) 821 (M + H)⁺; δ_H (400 MHz, CDCl₃) 2.61–3.82 (m, 24H, CH₂), 6.87 (s, 6H, CH=N), 7.83 (s, 6H, Py-3,3'-H), 7.98 (dd, 6H, *J*_{5,6} 5 Hz, Py-5,5'-H) and 8.92 (d, 6H, *J* 5 Hz, Py-6,6'-H).

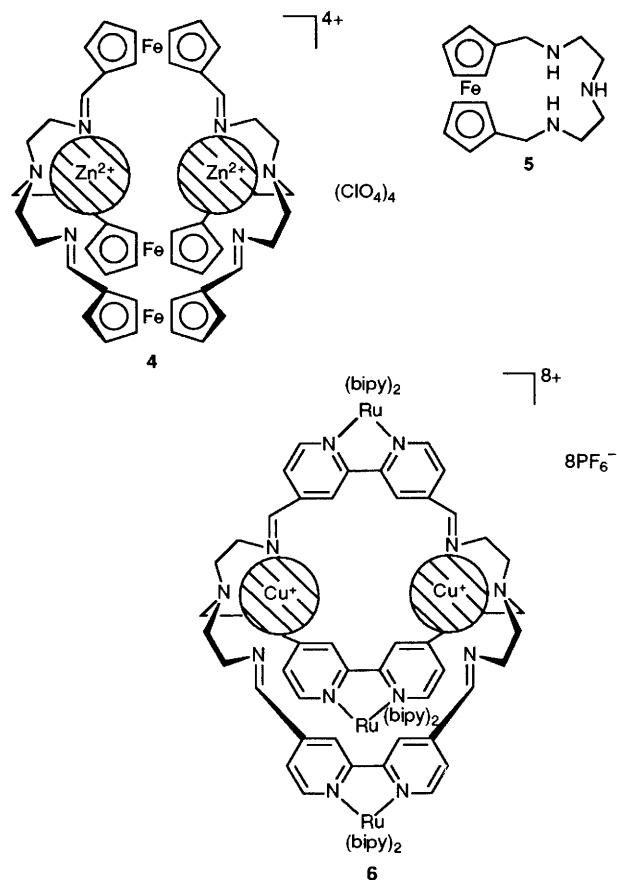
For L³ (Found: C, 64.3; H, 7.2; N, 21.55; C₄₈H₆₀N₁₄·CH₂Cl₂ requires C, 64.1; H, 6.6; N, 21.4%; *m/z* (FAB) 833 (M + H)⁺.

‡ For example [L¹Zn₂](ClO₄)₄, (Found: C, 39.9; H, 3.8; N, 7.85. C₄₈H₅₄Fe₃Cl₄N₈O₁₆Zn₂ requires C, 40.1; H, 3.8; N, 7.8%.)

[L³Zn₂](ClO₄)₄ (Found: C, 39.8; H, 4.8; N, 7.7. C₄₈H₆₀Fe₃Cl₄·N₈O₁₆Zn₂ requires C, 39.7; H, 4.6; N, 7.7%.)



tive ferrocene redox centres of both L^1 and L^3 to undergo irreversible oxidations. However, L^3 was found to be soluble in dichloromethane, L^1 was insoluble, and in this solvent a broad quasi-reversible oxidation wave ($E_p^a = 0.68$, $E_p^c = 0.52$ V) was observed. Coulometric experiments revealed this redox wave to correspond to a three-electron oxidation process. Addition of two equivalents of $Zn(dmsO)_5(ClO_4)_2$ to dichloromethane electrochemical solutions of L^3 resulted in a slight sharpening of the oxidation wave although no significant anodic shifts were observed. This result suggests the two coordinated Zn^{2+} guest cations are not electrostatically communicating to the ligand's peripherally linked ferrocene redox centres. In contrast **5** forms a $[(5)Zn](ClO_4)_2$ complex and does electrochemically recognise Zn^{2+} ; the reversible ferrocene-ferrocenium redox couple undergoes an anodic shift of 110 mV in acetonitrile solution. The reaction of three equivalents of $[RuCl_2(bipy)_2] \cdot 2H_2O$ ¹⁶ with one equivalent of L^2 in dimethylformamide initially gave an intensely coloured deep red solution. Treatment with an excess amount of ammonium hexafluorophosphate precipitated the trimetallic complex $[L^2Ru_3(bipy)_6](PF_6)_6$ containing three *externally* coordinated ruthenium(II) cations in quantitative yield.[§] The addition of two equivalents of $Cu(MeCN)_4PF_6$ ¹⁷ to an acetonitrile solution of the latter complex gave the novel heteropolymetallic complex $[L^2Ru_3(bipy)_6Cu_2](PF_6)_8$ **6**, containing two internally coordinated copper(I) cations in addition to the three externally bound ruthenium(II) cations. In an analogous stepwise synthetic procedure starting with L^4 the heteropolymetallic $[L^4Ru_3(bipy)_6Zn_2](PF_6)_8$ complex was



§ $[L^2Ru_3(bipy)_6](PF_6)_6$, (Found: C, 44.3; H, 3.4; N, 12.3. $C_{108}H_{96}N_{26}Ru_3P_6F_{36}$ requires C, 44.25; H, 3.3; N, 12.4%.)

also successfully isolated. Detailed absorption and emission spectroscopic and electrochemical investigations of these heteropolymetallic cryptates are in progress and preliminary results suggest the internally coordinated zinc(II) metal cations do electrostatically communicate and perturb the photo- and electro-chemical properties of the externally bound ruthenium(II) cations; for example the metal-to-ligand charge-transfer (MLCT) band of $[L^2Ru_3(bipy)_6](PF_6)_6$ is blue shifted in the presence of an excess amount of $Zn(ClO_4)_2$.

In conclusion these 'one-step' prepared novel multisite receptors containing either peripherally linked ferrocene redox centres or externally orientated 2,2'-bipyridyl transition metal recognition sites offer the future possibility of not only producing new homo- and hetero-polymetallic complexes of spectroelectrochemical interest but also of encapsulating organic guest substrates for supramolecular catalytic investigations.¹⁰

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