



Synthesis and complexation properties of novel triazolyl-based ferrocenyl ligands

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ABSTRACT

Two new ligand derivatives of ferrocene, namely *N*-4-[3,5-di-(2-pyridyl)-1,2,4-triazolyl]ferrocene carbimine (**L1**) and *N*-4-[3,5-di-(2-pyridyl)-1,2,4-triazolyl]ferrocene carbamide (**L2**), were synthesised in good yields by reacting the known compound 3,5-di-pyridine-2-yl-[1,2,4]triazol-4-ylamine (**1**) with ferrocenecarbaldehyde and chlorocarbonyl ferrocene, respectively. The structures of **L1** and **L2** were determined by X-ray crystallography. The complexation of **L1** and **L2** with Cu^I, Ag^I, Zn^{II} and Cd^{II} was studied by NMR and UV–vis spectroscopies, as well as by electrochemistry, with titrations used to determine metal:ligand stoichiometries. The cyclic voltammograms of **L1** and **L2** and their respective complexes indicated reversible one-electron transfers corresponding to the Fc^{0/+} redox couple (Fc = ferrocene), with formal electrode potentials shifting to more positive values upon metal complexation.

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1. Introduction

The self-assembled formation of well-defined metal-containing architectures is an ongoing topical area in supramolecular chemistry [1,2]. In particular, grid-type coordination arrays, which consist of a regular array of metal cations arranged between two perpendicular sets of parallel ligands, have been extensively studied over the past years [3–6]. The resulting compounds present interesting physico-chemical properties, such as electrochemical [7,8], optical [8], electronic [9], magnetic [10–12] or catalytic activity [13]. The choice of suitable ligands and metal ions is hence crucial for their synthesis. In the case of grids, the ligands used are normally planar and contain rigid linear spacers between the binding sites. The choice of metal ions employed depends on the number and type of coordinative sites of the ligand. Although the properties of self-assembled structures have been examined in detail, electrochemistry has seldom been used to follow their formation. One convenient method for doing this is to simply append or link re-

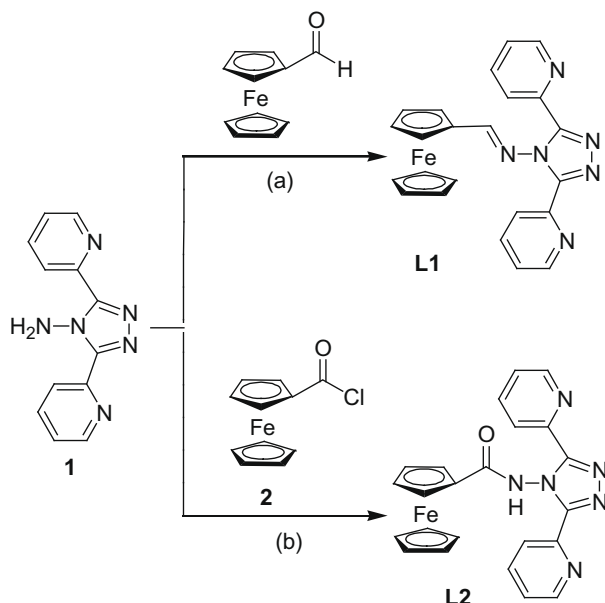
dox-active units to ligands that can form self-assembled complexes. Previously ferrocene has been utilised as a linker group between bipyridine and quinquepyridine ligands that form helicate complexes with metal ions [14,15]. More recently, the controlled self-assembly of ferrocene-containing heterobimetallic rhomboidal and hexagonal complexes and their associated electrochemistry were reported [16]. Here we report two new ligands (**L1** and **L2**, Scheme 1) bearing a ferrocene (Fc) unit that were designed primarily to investigate the possibility of forming novel redox-active assembled structures and to monitor the formation of these assemblies through electrochemical means. Furthermore, since it has previously been shown that the aggregation of ferrocene-containing surfactants can be controlled using the Fc^{0/+} redox couple [17,18], a secondary aim was to determine whether the strength of these inorganic assemblies could be controlled by the Fc redox state.

As shown by our [19,20] and other more recent [14,21–24] studies on ferrocene-containing metal complexes involving heterocyclic ligands, the ferrocene group is an ideal choice as a redox-active moiety due to the ease in which it can be functionalised with metal-binding ligands and its reversible electrochemistry. The coordinative unit selected for this work was a derivative of 3,5-di-pyridine-2-yl-[1,2,4]triazol-4-ylamine [25,26] (**1**, Scheme 1) and was chosen because tetrahedral complexes of 1:1 stoichiometry were anticipated to be not dissimilar to those obtained by Youinou et al. in [2 × 2] grid formation with 3,6-bis(2'-pyridyl)pyridazine

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Scheme 1. Synthesis of **L1** and **L2**. (a) $\text{H}_2\text{SO}_{4\text{conc}}$, 5 Å molecular sieves, toluene, reflux, 22 h, 56%. (b) Triethylamine, CH_2Cl_2 , 0 °C to r.t., 64 h, 59%.

[27]. Ligand **1** also presents the advantage of having a free amino group, which can be easily coupled to the ferrocene group in different ways.

Multinuclear complexes of Ag^{I} [28], Cd^{II} [29], Zn^{II} [29–32], Cu^{I} [33–36] and Fe^{II} [37] have previously been reported with 3,5-di-2-pyridyl-1,2,4-triazole and its derivatives. Chen et al. has also summarised the different 1:1 isomeric complexes with Cu^{I} in a tetrahedral coordination environment that can potentially form with this ligand in its deprotonated state [36]. These are chair, $[2 \times 2]$ grids, circular helicate, 4_1 helix, zigzag chain or 2_1 helix. In the case of ligands **L1** and **L2**, in line with previous studies on closely related ligands [30,38] and also due to the bulkiness of the ferrocene group, we anticipated that the nitrogen of the imine/amide groups and the adjoining nitrogen atom on the triazole were less likely to be coordinated. Therefore, in this study, *cis*-bridging $[2 \times 2]$ grids or polymeric helices were the only 1:1 complexes in a tetrahedral coordination environment that could reasonably be expected to form.

In this contribution, we report the facile synthesis and in-depth characterisation of ferrocene-containing ligands **L1** and **L2** (Scheme 1), including X-ray crystallographic studies. Their complexation with the metal ions Cu^{I} , Ag^{I} , Zn^{II} and Cd^{II} , as studied by NMR and UV–vis spectroscopies and by electrochemistry, is also reported.

2. Results and discussion

2.1. Synthesis and characterisation of ligands

Both ligands *N*-4-[3,5-di-(2-pyridyl)-1,2,4-triazolyl]ferrocene carbimine (**L1**) and *N*-4-[3,5-di-(2-pyridyl)-1,2,4-triazolyl]ferrocene carbamide (**L2**) were obtained in good yields by reacting the known compound 3,5-di-pyridine-2-yl-[1,2,4]triazol-4-ylamine [25,26] (**1**) with the commercially available ferrocenecarbaldehyde and the easy-to-prepare chlorocarbonyl ferrocene [39,40] (**2**), respectively (see Scheme 1). Interestingly, both ligands did not need to be purified by column chromatography. The main impurity of **L1**, ferrocenecarbaldehyde, could be easily washed away/recovered due to its solubility in hexane. The poor solubility of **L2** in dichloromethane allowed the effective removal of all impurities.

The formation of **L1** and **L2** was confirmed unambiguously by ^1H NMR spectroscopy with, for both ligands, the disappearance of the proton signal of the amine group of **1** at 8.51 ppm and the appearance of the imine proton of **L1** and amide proton of **L2** at 8.71 ppm and 10.84 ppm, respectively. Furthermore, the presence of **L1** and **L2** was further ascertained by ^{13}C NMR spectroscopy with two peaks at 173.02 ppm and 170.42 ppm corresponding to the imine carbon of **L1** and the amide carbon of **L2**, respectively.

2.2. X-ray crystallography studies [41]

Orange needles of **L1** suitable for X-ray analysis were grown by slow diffusion of ether into a solution of **L1** in dichloromethane. The crystallographic structure of **L1** (see Fig. 1) reveals classical interatomic and torsion angles for such types of bonds [42]. Hence, the average distance between the cation Fe^{2+} and the carbon atoms of the Cp ring (Cp = cyclopentadienyl) of ferrocene is about 2.04 Å and the angle between the two Cp planes is $0.7(2)^\circ$. Of interest for the purpose of this work, is the fact that the pyridine rings can rotate to allow the formation of the desired grid-type geometry.

Interestingly, two polymorphs were obtained during our attempts to crystallise **L2**. The first polymorph crystallised in the non-centrosymmetric orthorhombic space group *Fdd2*, with one molecule in the asymmetric unit, Fig. 2. The second crystallized in the centrosymmetric monoclinic space group *P2₁/c*, with two independent molecules per asymmetric unit, Fig. 3. It can be seen that there are significant structural differences between these two polymorphs. In the orthorhombic polymorph the two nitrogen atoms of the pyridine rings, N5 and N6, are oriented on the same side as the two nitrogen atoms of the triazole ring, N3 and N4. There are, therefore, no intramolecular $\text{N-H} \cdots \text{N}$ hydrogen bonds formed. Interestingly, Fig. 2 shows clearly that ligand **L2** has the ideal geometry to form the $[2 \times 2]$ grid-type complex with the two pyridine rings, which are almost co-planar with the triazole ring.

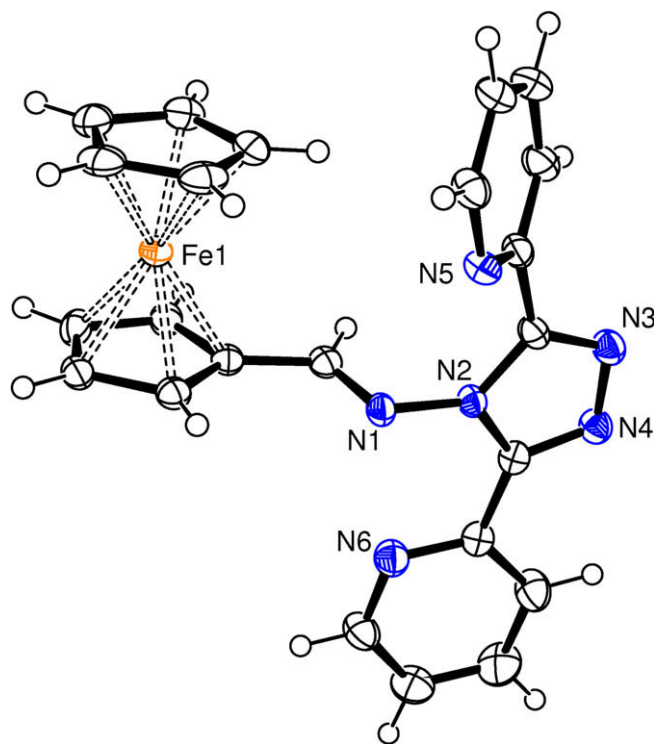


Fig. 1. ORTEP plot of **L1**, with thermal ellipsoids drawn at the 50% probability level.

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